

Superconductivity in fullerides

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Experimental studies of the superconductive properties of fullerides are briefly reviewed. Theoretical calculations of the electron-phonon coupling, in particular for the intramolecular phonons, are discussed extensively. The calculations are compared with coupling constants deduced from a number of different experimental techniques. It is discussed why A_3C_{60} are not Mott-Hubbard insulators, in spite of the large Coulomb interaction. Estimates of the Coulomb pseudopotential μ^* , describing the effect of the Coulomb repulsion on the superconductivity, as well as possible electronic mechanisms for the superconductivity, are reviewed. The calculation of various properties within the Migdal-Eliashberg theory and attempts to go beyond this theory are described. [S0034-6861(97)00702-2]

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I. INTRODUCTION

The fullerenes (C_{60} , C_{70} , . . .) have attracted much interest since their discovery by Kroto *et al.* (1985), not

least because of their appealing, symmetric shape (see Fig. 1). This interest increased dramatically when Krättschmer *et al.* (1990) discovered how to produce C_{60} in large enough quantities to make solids (fullerites) of a size that allowed traditional solid-state experiments. Very soon Haddon *et al.* (1991) found that intercalation of alkali-metal atoms in solid C_{60} leads to metallic behavior. Shortly afterwards it was found that some of these alkali-doped C_{60} compounds (fullerides) are superconducting with a transition temperature T_c that is only surpassed by the cuprates (Fleming *et al.*, 1991; Hebard *et al.*, 1991; Holczer, Klein, Huang, *et al.*, 1991; Rosseinsky *et al.*, 1991; Tanigaki *et al.*, 1991); Thus T_c is 33 K for $RbCs_2C_{60}$ (Tanigaki *et al.*, 1991), and for Cs_3C_{60} under pressure $T_c=40$ K has been reported (Palstra *et al.*, 1995). The great interest in the superconductivity of the alkali-doped C_{60} compounds is in particular due to these systems' being a completely new class of superconductors, the large value of their T_c , and the question of whether or not such a large value of T_c can be caused by the coupling to phonons alone. There has therefore been a great effort over the last five years to characterize and understand both the normal-state and the superconduct-

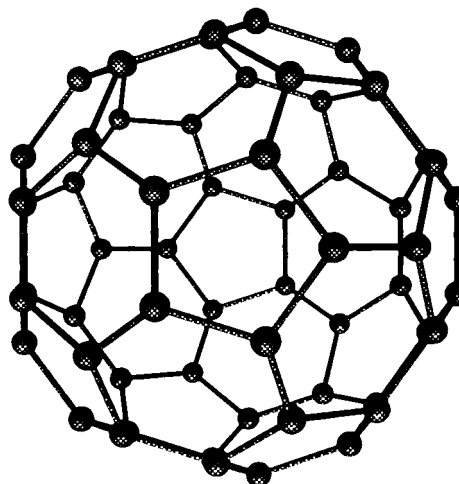


FIG. 1. The C_{60} molecule.

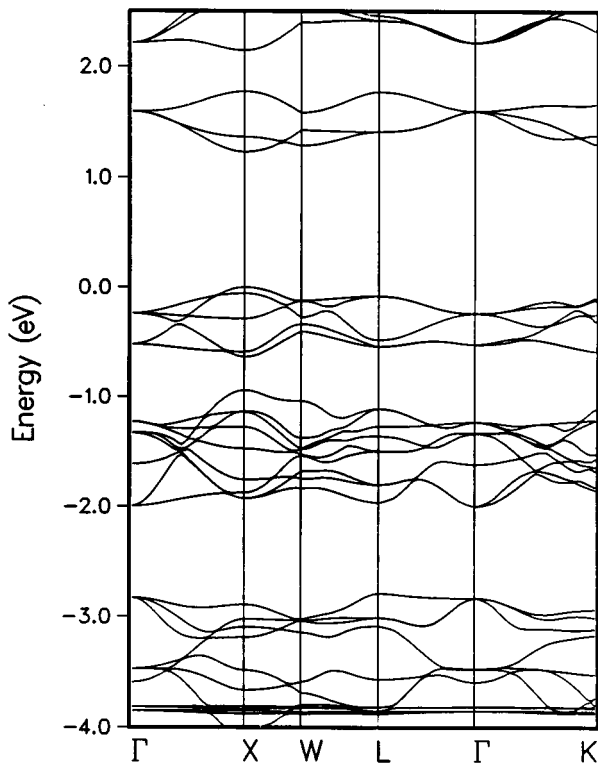


FIG. 2. Some of the subbands around the Fermi energy for solid C_{60} in the $Fm\bar{3}$ structure. The bands at about -0.5 eV are the h_u bands, which are occupied in solid C_{60} , and the bands at about 1.5 eV are the t_{1u} bands, which become populated in A_nC_{60} . The bands around -1.5 eV result from the overlapping h_g and g_g bands. From Erwin (1993).

ing properties of fullerides. The present review deals only with C_{60} compounds, since no other superconducting fullerides are known at present.

C_{60} is the most symmetric molecule in the sense that its point group (icosahedral) with 120 symmetry operations is the largest point group of the known molecules. It has the shape of a soccer ball. The 60 carbon atoms are all equivalent and form 12 pentagons and 20 hexagons.

The C_{60} molecules condense into a solid of weakly bound molecules. While the shortest separation between two atoms on the same molecule is about 1.4 Å, the shortest separation between two atoms on different molecules is about 3.1 Å. The fullerites are therefore molecular solids, in which many of the molecular properties essentially survive. The discrete levels of a free C_{60} molecule are only weakly broadened in the solid, which leads to a set of essentially nonoverlapping bands with a width of about $1/2$ eV, as is illustrated in Fig. 2. The system therefore has two very different energy scales, the intramolecular ($E_I \sim 30$ eV) and the intermolecular ($W \sim 1/2$ eV) energy scales. For an undoped C_{60} solid, the h_u band is full and the t_{1u} band is empty, and this system is therefore a band insulator. When solid C_{60} is doped by alkali atoms, the alkali atoms donate about one electron each to the t_{1u} band (Erwin and Pederson, 1991; Saito and Oshiyama, 1991b; Martins and Troullier,

1992; Satpathy *et al.*, 1992). Since the t_{1u} band can take six electrons, it is half-full for A_3C_{60} ($A=K, Rb$), which is a metal (Haddon *et al.*, 1991). A_4C_{60} is, however, an insulator (Kiefl *et al.*, 1992; Murphy *et al.*, 1992; Benning *et al.*, 1993), although the t_{1u} band is only partly filled and should be a metal according to band theory (Erwin, 1993; Erwin and Bruder, 1994). A_6C_{60} is a band insulator. Recently, AC_{60} has attracted much interest because of its possibly quasi-one-dimensional character (Chauvet *et al.*, 1994; Stephens *et al.*, 1994; Erwin *et al.*, 1995). TDAE- C_{60} has a ferromagnetic-like transition at $T=16$ K (Allemand *et al.*, 1991). If the fullerides are considered as organic compounds, then of all the organic compounds they have the highest superconducting and (ferro)magnetic transition temperatures.

In A_3C_{60} ($A=K, Rb$) the C_{60} molecules are located on a fcc lattice. At low temperatures, the C_{60} molecules take one of two likely orientations in an essentially random way (Stephens *et al.*, 1991). This orientational disorder has a substantial effect on some of the electronic properties (Gelfand and Lu, 1992a, 1992b, 1993; Mele and Erwin, 1994) but has been neglected in most calculations. A certain short-range correlation of the orientations is expected on theoretical grounds (Gunnarsson *et al.*, 1991; Mazin, Liechtenstein, *et al.*, 1993; Erwin and Mele, 1994) and has been observed experimentally (Teslic *et al.*, 1995). The alkali atoms are located in the tetrahedral and octahedral holes. In Rb NMR of Rb_3C_{60} one would then expect to observe two lines. At low temperatures, however, three lines are seen (Walstedt *et al.*, 1993; Zimmer *et al.*, 1993), raising some questions about our understanding of the precise structure of A_3C_{60} .

The effective Coulomb interaction between two electrons on a C_{60} molecule in a solid is about $1-1\frac{1}{2}$ eV (Antropov *et al.*, 1992; Brühwiler *et al.*, 1992; Lof *et al.*, 1992; Pederson and Quong, 1992). The long-ranged Coulomb interaction in the A_3C_{60} compounds leads to a charge-carrier plasmon, due to the oscillations of the t_{1u} electrons. This plasmon has the energy $\omega_{pl} \sim 1/2$ eV, an intermediate coupling constant $(g/\omega_{pl})^2 \sim 1$ (Antropov, Gunnarsson, and Liechtenstein, 1993; Knupfer *et al.*, 1993), and unusual dispersion (Gunnarsson, Eyert, *et al.*, 1996) and broadening (Liechtenstein *et al.*, 1996).

In systems where the superconductivity is driven by the electron-phonon interaction, the transition temperature T_c can be calculated in the Eliashberg (1960) theory. A simple estimate of T_c can be obtained from the McMillan (1968) formula

$$T_c = \frac{\omega_{ln}}{1.2} \exp \left[- \frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right], \quad (1)$$

where ω_{ln} is a typical phonon frequency (logarithmic average), λ is the electron-phonon coupling, and μ^* is the Coulomb pseudopotential, which describes the effects of the repulsive Coulomb interaction. To estimate T_c we then need to consider in particular λ and μ^* .

C_{60} has intramolecular vibrations (phonons) with energies up to $\omega_{ph} \sim 0.2$ eV. Only phonons with A_g or H_g

symmetry couple to the t_{1u} electrons. It was very early proposed that these phonons drive the superconductivity (Varma *et al.*, 1991; Mazin *et al.*, 1992; Schluter *et al.*, 1992a, 1992b). Estimates of the electron-phonon interaction $\lambda \sim \frac{1}{2}-1$ fall in the right range to explain the experimental values of T_c . It has therefore become widely, but not universally, accepted that the intramolecular H_g phonons drive the superconductivity. Other phonon modes, such as librations (oscillatory rotational motion), C_{60} - C_{60} vibrations, and alkali- C_{60} vibrations, are believed to play a small role in the superconductivity. It has, however, also been argued that an electronic mechanism may drive the superconductivity (Baskaran and Tosatti, 1991; Chakravarty *et al.*, 1991; Friedberg *et al.*, 1992).

The attractive interaction between two electrons induced by the electron-phonon interaction is small ($\sim 1/10$ eV) compared with the Coulomb repulsion between two electrons on the same C_{60} molecule ($U \sim 1-1\frac{1}{2}$ eV). Nevertheless, for conventional superconductors it is argued that the effects of the Coulomb interaction are drastically reduced by retardation effects, due to the very different energy scales for phonons and electrons. The dimensionless Coulomb pseudopotential μ^* is therefore believed to be drastically renormalized for such systems. For doped C_{60} solids it has been controversial whether the intramolecular (E_I) or intermolecular (W) (Anderson, 1991) energy scale is relevant for the retardation effects. In the latter case one may expect the retardation effects to be small, since $\omega_{ph} \sim W$. It has therefore been asserted that the phonons alone cannot explain the superconductivity in A_3C_{60} (Anderson, 1991). Later work has provided support for the intermolecular energy scale's being the relevant one but nevertheless has found that the electron-phonon mechanism may be sufficient if the Coulomb interaction is screened as efficiently as predicted by the random-phase approximation (RPA) (Gunnarsson and Zwicknagl, 1992).

In the A_3C_{60} ($A=K, Rb$) compounds many energy scales are similar, $\omega_{ph} \sim \tilde{E}_{JT} \lesssim \omega_{pl} \sim W \lesssim U$, where \tilde{E}_{JT} is the Jahn-Teller energy of C_{60}^{-3} , which may be of the order of several tenths of an eV. Furthermore, certain coupling constants are intermediate, $\lambda \sim 1$, $(g/\omega_{pl})^2 \sim 1$. This is a situation in which we may expect particularly interesting physics but also a situation that is particularly difficult to treat theoretically. $W < U$ suggests very strong correlation effects (Lof *et al.*, 1992), which have, however, not been considered in most treatments of fullerides. The similar magnitudes of ω_{ph} and W raise doubt about the strength of the retardation effects, as discussed above, and they imply that Migdal's theorem is not valid. Corrections to Migdal's theorem have been considered in a few cases (see, for example, Pietronero and Strässler, 1992; Takada, 1993; Pietronero *et al.*, 1995). Jahn-Teller-like effects, beyond what is included in the Migdal theory, may also play a role (Auerbach *et al.*, 1994; Manini *et al.*, 1994). The fact that \tilde{E}_{JT} may not be much smaller than W could also be important for the insulating character of A_4C_{60} (Fabrizio and Tosatti, 1996). In view of this, it is not surprising that many of

TABLE I. Structure, valence, and band involved for certain classes of fulleride superconductors. (A =alkali (K,Rb,Cs) metal, AE=alkaline earth, RE=rare earth.)

Class	Structure	Valence
A_3C_{60}	$Fm\bar{3}m$	$n=3$ (t_{1u})
$Na_2A_xC_{60}$	$Pa3$	$n \leq 3$ (t_{1u})
$A_{3-x}Ba_xC_{60}$	$Fm\bar{3}m$	$n \geq 3$ (t_{1u})
$(AE)_xC_{60}$	$Im\bar{3}$, sc, orthorhomb	$n > 6$ (t_{1g})
$(RE)_xC_{60}$	Orthorhomb	

the normal-state properties are unusual (see, for example, Sawatzky, 1995) and several interesting, unresolved questions remain.

There have been a number of reviews of the fullerides. Several articles appeared in *Journal of Chemical Physics Solids* Vol. 53, No. 12 (Fischer and Cox, 1992), in Vol. 30 No. 8 of *Carbon* (1992), in Vol. 48 of *Solid State Physics* (e.g., Pickett, 1994; Lieber and Zhang, 1994), and in a book edited by Billups and Ciufolini (1993). Early reviews were those of Weltner and van Zee (1989), Kroto *et al.* (1991), Loktev (1992), and Wilson *et al.* (1992). A number of conference proceedings have appeared (Hammond and Kuck, 1992; Fischer *et al.*, 1993; Kumar *et al.*, 1993; Kuzmany *et al.*, 1993; Kuzmany, Fink, *et al.*, 1994, 1995; Prassides *et al.*, 1994). The field has further been reviewed by Holczer and Whetten (1992) and by Ramirez (1994) from an experimental and by Gelfand (1994) from a theoretical point of view. A general review with the emphasis on the superconductivity was given by Hebard (1992). Specific topics have recently been reviewed by Golden *et al.* (1995; high-energy spectroscopies), Kuzmany, Winkler, and Pichler (1995; infrared spectroscopies), Pintschovius (1996; neutron scattering), Kuzmany, Matus, *et al.* (1994; Raman scattering), and Buntar and Weber (1996; magnetic properties). The theory of superconductivity in general has been presented in several textbooks, e.g., those of Schrieffer (1964), Parks (1969), and Tinkham (1975), and in reviews, e.g., Allen and Mitrovic (1982) and Carbotte (1990), and it will not be addressed here. Popular descriptions of the fullerenes have been given by Baggot (1994) and Aldersey-Williams (1995).

II. EXPERIMENTAL RESULTS

A. Transition temperature

The superconducting fullerides may be divided into five classes: (1) A_3C_{60} , where $A=K, Rb, Cs$, or some combination of these elements; (2) $Na_2A_xC_{60}$ ($x \leq 1$) (3) $A_{3-x}Ba_xC_{60}$, (4) Ca_xC_{60} ($x \sim 5$) (Kortan *et al.*, 1992a), Ba_6C_{60} (Kortan *et al.*, 1992b) or Ba_4C_{60} (Baenitz *et al.*, 1995), and Sr_6C_{60} (Kortan *et al.*, 1994); and (5) $Yb_{2.75}C_{60}$ and Sm_xC_{60} . A summary is given in Table I.

These classes differ in particular in their structure and the C_{60} valence. In the first class and in the second class with $x=1$, three electrons are doped into the t_{1u} band,

while in the second class with $x < 1$, the valence is smaller than three. In the third class the filling of the t_{1u} band is larger than three, and in the fourth class the t_{1u} band is full and the t_{1g} band is populated (Y. Chen *et al.*, 1992; Wertheim *et al.*, 1992; Erwin and Pederson, 1993; Saito and Oshiyama, 1993; Knupfer *et al.*, 1994). The t_{1g} states furthermore strongly hybridize with alkaline-earth states (Y. Chen *et al.*, 1992; Erwin and Pederson, 1993; Saito and Oshiyama, 1993), in contrast to the very weak hybridization of the t_{1u} states with the alkali states in A_3C_{60} .

In the first three classes, the C_{60} molecules are located on a fcc lattice. The first (Stephens *et al.*, 1991) and third (Yildirim, Barbedette, Fischer, Bendele, *et al.*, 1996) classes have the space group $Fm\bar{3}m$, and the molecules more or less randomly take one of two preferential orientations. In the second class the space group is $Pa\bar{3}$ (Kniaz *et al.*, 1993; Prassides *et al.*, 1994), possibly with some distortions for Na_2KC_{60} and Na_2RbC_{60} (Maniwa *et al.*, 1995). For these systems there are four C_{60} molecules per unit cell, all having different orientations. In the fourth group Ca_5C_{60} has a simple cubic structure with the molecules at the fcc lattice positions (Kortan *et al.*, 1992a), Ba_4C_{60} has an orthorhombic structure (Baenitz *et al.*, 1995), while Ba_6C_{60} (Kortan *et al.*, 1992b) and Sr_6C_{60} (Kortan *et al.*, 1994) have a bcc structure ($Im\bar{3}$).

The critical temperature T_c as a function of the lattice parameter a has been determined by a large number of groups for both the first class (Fleming *et al.*, 1991; Sparn *et al.*, 1991; Tanigaki *et al.*, 1991; Zhou *et al.*, 1992) and the second (Tanigaki *et al.*, 1992; Mizuki *et al.*, 1994; Yildirim, Fischer, *et al.*, 1995) (for $x=1$) class. In Fig. 3 these results are summarized. The figure illustrates that in the first class T_c varies smoothly with a , relatively independently of the alkali atoms in the compound. Thus, if pressure is applied to Rb_3C_{60} to give the same a as for K_3C_{60} at normal pressure, the corresponding T_c 's are approximately equal (Zhou *et al.*, 1992). It is therefore the lattice parameter, not the alkali atom, which determines T_c . This seems to exclude the alkali vibrations as the main driving force for the superconductivity, since the vibration frequency and thereby T_c would then be expected to depend on the mass of the alkali atoms. Recent work has, however, questioned these results, finding a different pressure-volume relation for Rb_3C_{60} than the earlier work and thereby a different $T_c - a$ dependence (Diederichs *et al.*, 1997). A certain deviation between Rb_2CsC_{60} under pressure and Rb_3C_{60} was also observed by Schirber *et al.* (1993). This would imply that changing the lattice parameter by physical or chemical pressure does not lead to identical results, although the deviations are not dramatic. A smooth variation with lattice parameter is observed for the second group ($x=1$) (see Fig. 3). It is, however, interesting that the slopes of the two classes are very different.

$(NH_3)_4Na_2CsC_{60}$ probably also belongs to the first class (with the likely structure $Fm\bar{3}$ or $Fm\bar{3}m$), and its

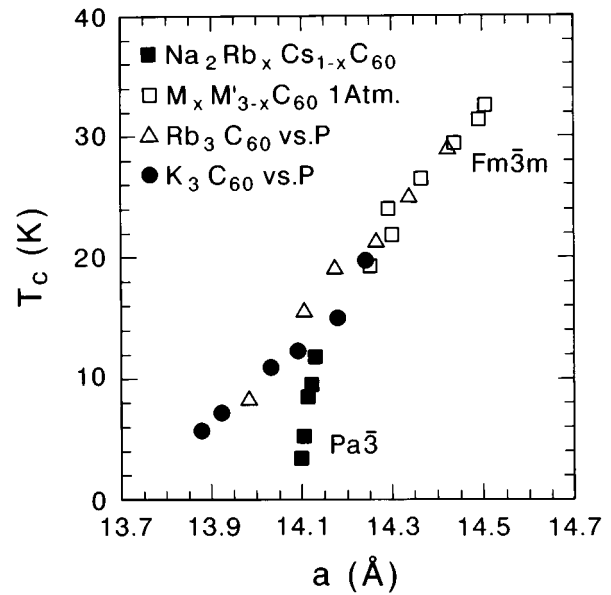


FIG. 3. T_c as a function of the lattice parameter a for the $Fm\bar{3}m$ (triangles, circles, and open squares) and $Pa\bar{3}$ (filled squares) superconductors. For K_3C_{60} and Rb_3C_{60} the lattice parameter was varied by changing the pressure, while for $M_xM'_{3-x}C_{60}$ (with $M, M' = K, Rb, Cs$) the lattice parameter was varied by changing the composition. After Yildirim, Fischer, *et al.* (1995).

$T_c = 29.6$ K is essentially what one would expect from the large lattice parameter $a = 14.473$ Å (Zhou *et al.*, 1993). Cs_3C_{60} has a different (noncubic) structure and a different pressure dependence than the other A_3C_{60} compounds, and it should not be considered as a member of the first class. The maximum T_c found for Cs_3C_{60} is 40 K (Palstra *et al.*, 1995). Another interesting system is $NH_3K_3C_{60}$, which like K_3C_{60} has three electrons in the t_{1u} orbital but an orthorhombic distortion of the fcc lattice (Rosseinsky *et al.*, 1993; Zhou *et al.*, 1995). At ambient pressure this system shows no superconductivity above 4 K, and it is possibly an insulator. Under pressure, however, superconductivity occurs with a maximum observed T_c of 28 K. It had been suggested that only cubic fullerides can be superconductors, but Cs_3C_{60} and $NH_3K_3C_{60}$ under pressure now provide examples of noncubic superconducting fullerides. These compounds nevertheless raise interesting questions about the role of the deviation from cubic symmetry, since the application of pressure reduces this symmetry lowering and increases T_c (Palstra *et al.*, 1995; Zhou *et al.*, 1995). Alternatively, the closeness to a Mott transition may be important for the pressure dependence (Palstra *et al.*, 1995; Zhou *et al.*, 1995).

Yildirim, Barbedette, Fischer, Lin, *et al.* (1996) have studied $Na_2Cs_xC_{60}$ for $x = 0.25, 0.50, \text{ and } 0.75$. The values of T_c found for these compounds are shown in Fig. 4 as a function of the expected valence $n = 2 + x$. It is found that T_c drops quickly as the valence is reduced. For $n = 2.5$ no superconductivity was observed above $T = 0.5$ K, and the systems are believed to be metallic down to $n = 2.25$.

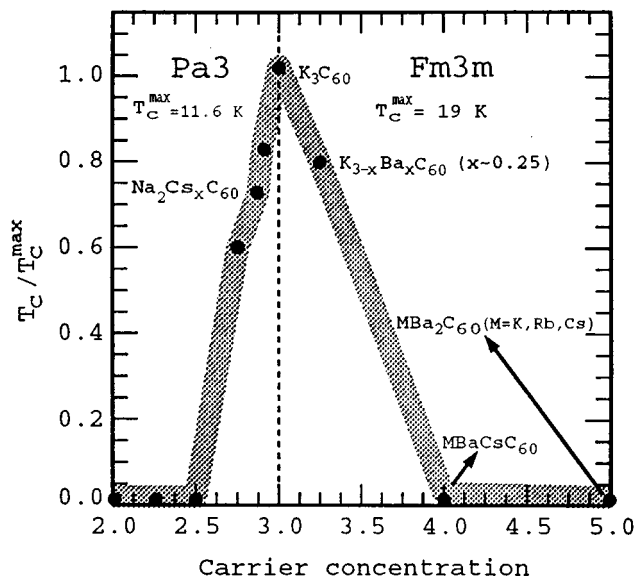


FIG. 4. T_c as a function of carrier concentration per C_{60} molecule (C_{60} valence n) for the $Na_2Cs_xC_{60}$ ($x \leq 1$, $n \leq 3$) and $K_{3-x}Ba_xC_{60}$ ($n \geq 3$) compounds. T_c is scaled by the T_c (T_c^{\max}) of the end members Na_2CsC_{60} and K_3C_{60} . The heavy line is a guide for the eye. Observe the different lattice structures. After Yildirim, Barbedette, Fischer, Lin, *et al.* (1996).

Yildirim *et al.* [Yildirim, Barbedette, *et al.*, 1995; Yildirim, Barbedette, Fischer, Lin, *et al.* (1996), and Yildirim, Barbedette, Fischer, Bendele, *et al.* (1996)] studied $Rb_{3-x}Ba_xC_{60}$ for $x=0.25, 1$, and 2 . Based on Raman data and theoretical considerations, they concluded that the C_{60} valence is $n=3+x$ and that Ba is essentially completely ionized. The results for T_c are shown in Fig. 4. T_c drops rapidly with x , and for $x=1$ ($n=4$) and $x=2$ ($n=5$) no superconductivity was observed above $T=0.5$ K. These compounds show a very small Pauli susceptibility, and it was tentatively concluded that they are weakly metallic (Yildirim, Barbedette, Fischer, Bendele, *et al.*, 1996). Figure 4 suggests a rapid drop of T_c when the C_{60} valence deviates from 3. The reduction for $n>3$, but not for $n<3$ (see Sec. VII.A.2), may be explained by the reduction of the density of states with increasing filling, once the merohedral disorder is taken into account (Yildirim, Barbedette, *et al.*, 1995). The reduction of T_c as n is reduced below 3 seems not to be understood. Figure 4 furthermore appears to be inconsistent with the conclusion that stoichiometric A_3C_{60} is an insulator (Lof *et al.*, 1992). In such a case one might expect T_c to increase when the occupancy of the t_{1u} orbital moves away from integer values, in analogy with the high- T_c superconductors, while Fig. 4 shows the opposite trend.

In the fourth group the measured transition temperatures are 8.4 K (Ca_xC_{60}), 4 K (Sr_xC_{60}), and 7 K (Ba_xC_{60}).

Recently, superconductivity has been found in RE_xC_{60} , where RE is a rare-earth atom. Özdas *et al.* (1995) discovered that $Yb_{2.75}C_{60}$ is superconducting with $T_c=6$ K. This system has a slight orthorhombic distor-

tion of the $Pa\bar{3}$ structure into the $Pcab$ structure. Based on EXAFS measurements, it was concluded that Yb is divalent, which would imply a C_{60} valence of 5.5 (Özdas *et al.*, 1995). X. H. Chen and Roth (1995) found superconductivity in Sm_xC_{60} ($x<3$) with $T_c=8$ K.

It is also interesting to observe that Li_2AC_{60} is not superconducting (Hirosawa *et al.*, 1994). This system has a different structure from Na_2AC_{60} and A_3C_{60} . It has the space group $Fm\bar{3}m$, but with an orientational state of C_{60} that is best modeled as a quasispherical unit (Hirosawa *et al.*, 1994).

B. Superconductivity gap

The superconductivity gap Δ is of great interest, since a value of the reduced gap $2\Delta/T_c$ that is substantially larger than the BCS value (3.53) indicates that strong-coupling effects are important. For intermediate coupling, it is found that (Mitrovic *et al.*, 1984) [see also Carbotte (1990) for a discussion]

$$\frac{2\Delta}{T_c} = 3.53 \left[1 + 12.5 \left(\frac{T_c}{\omega_{\ln}} \right)^2 \ln \left(\frac{\omega_{\ln}}{2T_c} \right) \right], \quad (2)$$

where ω_{\ln} is the logarithmic average phonon frequency. This formula says that the deviation from the BCS result is small if $T_c/\omega_{\ln} \ll 1$. An early measurement of Δ was performed using point-contact tunneling in scanning tunneling microscopy, which gives $2\Delta/T_c=5.3$ for Rb_3C_{60} (Z. Zhang *et al.*, 1991). Later scanning tunneling microscopy measurements on single crystals have given reduced gaps $2\Delta/T_c=5.4$ (Jess *et al.*, 1994) and $2\Delta/T_c=2.0-4.0$ (Jess *et al.*, 1996). The variations in $2\Delta/T_c$ were ascribed to variations in the local stoichiometry at the tip position. From NMR measurements the values 3.0 for K_3C_{60} and 4.1 for Rb_3C_{60} (Tycko *et al.*, 1992), 4.3 for K_3C_{60} (Sasaki *et al.*, 1994), and 3.4 ± 0.2 K_3C_{60} (Auban-Senzier *et al.*, 1993) were deduced. Recent NMR measurements were found to be in good agreement with the BCS value for the gap (Stenger *et al.*, 1995). Using muon spin relaxation measurements, Kiefl *et al.* (1993) obtained the value 3.6 for Rb_3C_{60} . Recent optical measurements have given the values 3.44 for K_3C_{60} and 3.45 for Rb_3C_{60} (Degiorgi *et al.*, 1994; Degiorgi, 1995). The reduced gap was also measured in photoemission, giving the value 4.1 for Rb_3C_{60} (Gu *et al.*, 1994). Recent tunneling and optical studies found the reduced gap 4.2 ± 0.2 (Koller *et al.*, 1996) We note that the data obtained from different experiments show substantial variation ranging from the BCS value up to about 4.2.

C. Isotope effect

The isotope effect may provide interesting information about the mechanism for superconductivity. In the BCS theory for a system with only one type of ion with mass M , the transition temperature behaves as $T_c \sim M^{-\alpha}$, where $\alpha=0.5$. For the A_3C_{60} compounds, the C_{60} phonons are expected to be the important ones, and

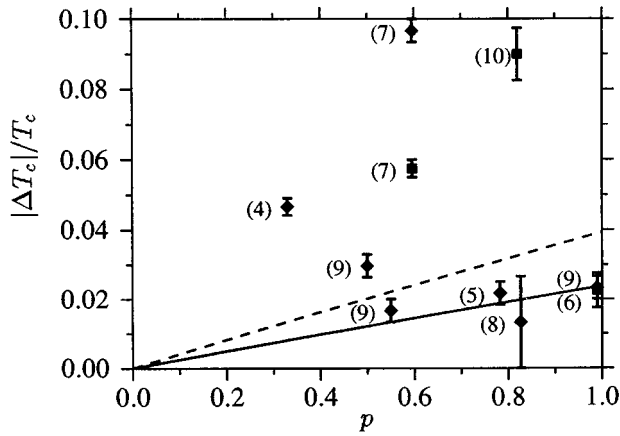


FIG. 5. The isotope shift ΔT_c of T_c for K_3C_{60} (squares) and Rb_3C_{60} (diamonds) as a function of the fraction p of the substitution ($p=1$ is completely ^{13}C). The dashed line shows the BCS result $\alpha=0.5$ and the full line $\alpha=0.3$. The results are obtained from (4) Ebbesen *et al.* (1992a, 1992b), (5) Ramirez, Kortan, *et al.* (1992), (6) Chen and Lieber (1992), (7) Zakhidov *et al.* (1992), (8) Bethune *et al.* (1992), (9) Chen and Lieber (1993), and (10) Auban-Senzier *et al.* (1993). After Deaven and Rokhsar (1993).

one is therefore interested in the isotope effect when ^{12}C is substituted by ^{13}C . For the case of complete (99%) substitution, it was found that $\alpha=0.30\pm 0.06$ for K_3C_{60} (C.-C. Chen and Lieber, 1992) and $\alpha=0.30\pm 0.05$ for Rb_3C_{60} (C.-C. Chen and Lieber, 1993). Interesting and contradictory results have been obtained for incomplete substitution. C.-C. Chen and Lieber (1993) found that for a single-peak mass distribution of C_{60} molecules [$Rb_3(^{13}C_{0.55}^{12}C_{0.45})_{60}$], the value of α was consistent with the result for complete substitution. On the other hand, they found that a two-peak mass distribution [$Rb_3(^{13}C_{60})_{0.5}(^{12}C_{60})_{0.5}$] gave a much larger value of α (~ 0.8). A value of α which is larger than 0.5 is unusual, but it was also observed by three other groups. Ebbesen *et al.* (1992a) obtained $\alpha=1.4\pm 0.5$ for Rb_3C_{60} (33% substitution), Zakhidov *et al.* (1992) obtained $\alpha=(1.2-1.43)\pm 0.2$ for K_3C_{60} and $\alpha=(2-2.25)\pm 0.25$ for Rb_3C_{60} (60% substitution), and Auban-Senzier *et al.* (1993) obtained $\alpha=1.45\pm 0.3$ for 82% substitution. However, these results were observed for distributions of C_{60} masses with essentially only one peak, while the $\alpha>0.5$ was obtained by C.-C. Chen and Lieber (1993) for a two-peak distribution. Finally Ramirez, Kortan, *et al.* (1992) obtained $\alpha=0.37\pm 0.05$ for a mass distribution of 15% $^{12}C_{60}$ and the rest ($^{13}C_{0.9}^{12}C_{0.1}$) $_{60}$. For the partially substituted compounds, the experimental situation thus appears to be unclear. The results are summarized in Fig. 5. The theoretical considerations have so far, however, been made for completely substituted systems, where $\alpha=0.3$ should be the best available experimental result. The theoretical treatment of partially substituted compounds remains a challenging problem.

The isotope effect with respect to the alkali dopants has also been studied. It was found that within the experimental uncertainty there is no isotope effect (Ebbe-

sen *et al.*, 1992b; Burk, Crespi, Fuhrer, *et al.*, 1994; Burk, Crespi, Zettl, *et al.*, 1994). This is consistent with the experimental result that applying pressure to Rb_3C_{60} so that the lattice parameter is reduced to that of K_3C_{60} leads to about the same T_c for both systems (Fleming *et al.*, 1991). This strongly suggests that the alkali ions have a very weak influence on T_c except for the indirect influence via the lattice parameter.

D. Other properties

A_3C_{60} is a type-II superconductor. The lower critical field H_{c1} has been measured to be 130 Oe (Holczer, Klein, Grüner, *et al.*, 1991) for K_3C_{60} and 120 Oe (Spurn *et al.*, 1992) and 60 ± 5 Oe (Ramirez *et al.*, 1994) for Rb_3C_{60} . To estimate the penetration depth $\lambda(0)$, one can now use the relationship (Tinkham, 1975)

$$H_{c1} = \frac{\phi_0}{4\pi\lambda(0)^2} \ln\left(\frac{\lambda(0)}{\xi_{GL}}\right), \quad (3)$$

where $\phi_0 = hc/e$ and ξ_{GL} is the Ginzburg-Landau coherence length. Putting $\xi_{GL} = 30 \text{ \AA}$, which is reasonable in view of the results below, one obtains the values $\lambda(0) = 2500 \text{ \AA}$ for K_3C_{60} and 2600 and 3700 \AA for Rb_3C_{60} . The penetration depth has also been estimated from muon spin resonance (μ SR), with the results 4800 \AA for K_3C_{60} and 4200 \AA for Rb_3C_{60} (Uemura *et al.*, 1991, 1993), and from the optical conductivity, with the result 8000 \AA for both K_3C_{60} and Rb_3C_{60} (Degiorgi *et al.*, 1992), and from NMR data, which gives 6000 \AA for K_3C_{60} and 4600 \AA for Rb_3C_{60} (Tycko *et al.*, 1992). Uemura *et al.* (1991) also deduced the temperature dependence of the penetration depth $\lambda(T)$. They could fit these results with the formula $[1 - (T/T_c)^\alpha]$, with $\alpha=3.2$. From this they concluded that K_3C_{60} probably is an isotropic s -wave superconductor, as expected. Based on values for $\lambda(0)$ and ξ , Uemura *et al.* (1991) also estimated an "effective" Fermi temperature T_F^{eff} . Combining their small value (470 K) for T_F^{eff} with T_c in a T_c vs T_F^{eff} plot, they found that A_3C_{60} belongs to a group of "exotic" superconductors that includes the high- T_c cuprates and the organic BEDT systems.

The upper critical field $H_{c2}(0)$ is of interest, since it allows an estimate of the coherence length via (Tinkham, 1975)

$$H_{c2}(0) = \frac{\phi_0}{2\pi\xi_{GL}}. \quad (4)$$

Several groups have measured $H'_{c2} \equiv dH_{c2}/dT$ and then obtained the value of $H_{c2}(0)$ from the Wertheimer-Helfand-Hohenberg (Wertheimer *et al.*, 1966) theory. Based on this, ξ_{GL} was deduced to be 26 \AA for K_3C_{60} (Holczer, Klein, Grüner, *et al.*, 1991) and 20 \AA for Rb_3C_{60} (Spurn *et al.*, 1992) from dc magnetization. The high-field susceptibility gave the values 29 \AA to 33 \AA (Boebinger *et al.*, 1992) and 35 \AA (Holczer and Whetten, 1992) for K_3C_{60} and 30 \AA (Holczer and Whetten, 1992) for Rb_3C_{60} . From the ratio ξ_{GL}/λ , it is clear that

TABLE II. Superconducting parameters for K_3C_{60} and Rb_3C_{60} . (Mainly after Ramirez, 1994).

Property	K_3C_{60}	Rb_3C_{60}
T_c	19.5 K	29.5 K
λ (μ SR)	4800 ± 200 Å	4200 Å
λ (optical)	8000 ± 500 Å	8000 ± 500 Å
λ (NMR)	6000 Å	4600 Å
ξ_0 (χ_{ac})	29–35 Å	30 Å
$\Delta C/T_c$	64 ± 14 mJ/mole-K ²	75 ± 14 mJ/mole-K ²
$2\Delta/k_b T_c$ (NMR)	3.0	4.1
$2\Delta/k_b T_c$ (optical)	3.44	3.45, 4.1
$2\Delta/k_b T_c$ (μ SR)		3.6 ± 0.3
$2\Delta/k_b T_c$ (tunneling)	5.3 ± 0.2	5.2 ± 0.3
$2\Delta/k_b T_c$ (tunneling)		4.3

A_3C_{60} is a type-II superconductor. The magnetic properties of the C_{60} superconductors have been reviewed by Buntar and Weber (1996).

The jump in the specific heat at T_c was estimated by Ramirez, Rosseinsky, *et al.* (1992) to be $\Delta C = 68 \pm 13$ mJ/mole-K² for K_3C_{60} and by Burkhart and Meingast (1996) to be 64 ± 14 and 75 ± 14 mJ/mole-K² for K_3C_{60} and Rb_3C_{60} , respectively. The Hebel-Slichter peak was not seen in early NMR measurements (Tycko *et al.*, 1992), but has been seen in μ SR (Kiefl *et al.*, 1993) and more recent NMR (Stenger *et al.*, 1995) measurements. The vertex-glass and vertex-fluid phase diagram of A_3C_{60} has been studied by Lin *et al.* (1994).

In Table II we have summarized some superconducting parameters. The table has mainly been extracted from Ramirez (1994), but it has been partly updated in the view of newer experiments.

III. PHONONS AND ELECTRON-PHONON COUPLING

The phonons and the electron-phonon interaction are very important for the properties of alkali fullerides. The electron-phonon interaction is usually assumed to cause the superconductivity. It should, however, also be important for the transport properties in general and may also play a substantial role for other electronic properties.

The phonons of alkali fullerides can be divided into subgroups that reflect the molecular nature of the solid. The highest modes are due to intramolecular vibrations and have energies in the range 273 – 1575 cm⁻¹ (0.034–0.195 eV) for an undoped C_{60} solid (Bethune *et al.*, 1991). The intermolecular phonons occur at substantially lower energies in the range up to about 140 cm⁻¹ (17 meV; Prassides *et al.*, 1991; Pintschovius, 1996). These modes contain both C_{60} - C_{60} and A - C_{60} ($A=K, Rb$) vibrations. Finally, there are librations, which occur at an energy of about 4–5 meV (Christides *et al.*, 1992; Schober *et al.*, 1994). These various phonons are schematically illustrated in Fig. 6. It is believed that the intramolecular modes play the main role in the supercon-

ductivity. We therefore focus on these modes, but the other modes are also discussed.

A. Intramolecular modes

For the intramolecular phonons, the effects of the interactions between the C_{60} molecules are small. These phonons can therefore be approximately classified by the icosahedral point group. In alkali fullerides, the t_{1u} band is (partly) populated. The coupling of the phonons to this band is therefore of particular interest. From symmetry arguments, it follows that the two phonons with A_g and the eight phonons with H_g symmetry can couple (Lannoo *et al.*, 1991; Varma *et al.*, 1991). We therefore focus our interest on these modes.

1. Calculations of phonon frequencies

There have been a number of calculations of the phonon frequencies. In Table III we show the results of calculations using the semiempirical MNDO (Modified Neglect of Differential Overlap) method (Varma *et al.*, 1991), an empirical force-constant model (Jishi *et al.*, 1992), and the *ab initio* density-functional method (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) in the local-density approximation (LDA) but using different numerical methods (Antropov, Gunnarsson, and Liechtenstein, *et al.*, 1993; Faulhaber *et al.*, 1993; Quong *et al.*, 1993). These calculations were all for a free C_{60} molecule, except the one by Antropov, Gunnarsson, and Liechtenstein, (1993), which was for K_3C_{60} in the so-called unidirectional structure, where all C_{60} molecules have the same orientation (where a cubic axis and a twofold molecular axis coincide). These calculations can be considered as representative for the large number of calculations that have been performed (see also Negri *et al.*, 1988; Adams *et al.*, 1991; Jones *et al.*, 1992; Kohanoff *et al.*, 1992; Onida and Benedek, 1992; Bohnen *et al.*, 1995). These results are compared with experimental results obtained from Raman scattering by Bethune *et al.* (1991). We can see that the best empirical and *ab initio* calculations have errors of the order of one percent. The small errors in, for instance, the calculations of Quong *et al.* (1993) suggest that the LDA errors for the frequencies are small. Bohnen *et al.* (1995) have calculated the changes in the phonon frequencies when going from solid C_{60} to K_3C_{60} and found a softening of the modes, in particular the high-frequency ones.

The four highest modes are primarily made up of vibrations tangential to the C_{60} surface, while the three lowest modes have mainly a radial character (Schluter *et al.*, 1992a, 1992b; Antropov, Gunnarsson, and Liechtenstein, 1993), as indicated in Fig. 6. The reason is that the molecule is much stiffer against tangential than radial distortions, since the former require larger bond-length changes. The phonon frequencies are high, extending up to about 0.2 eV. This is due to both the light mass of carbon and to the stiffness of the C—C bond.

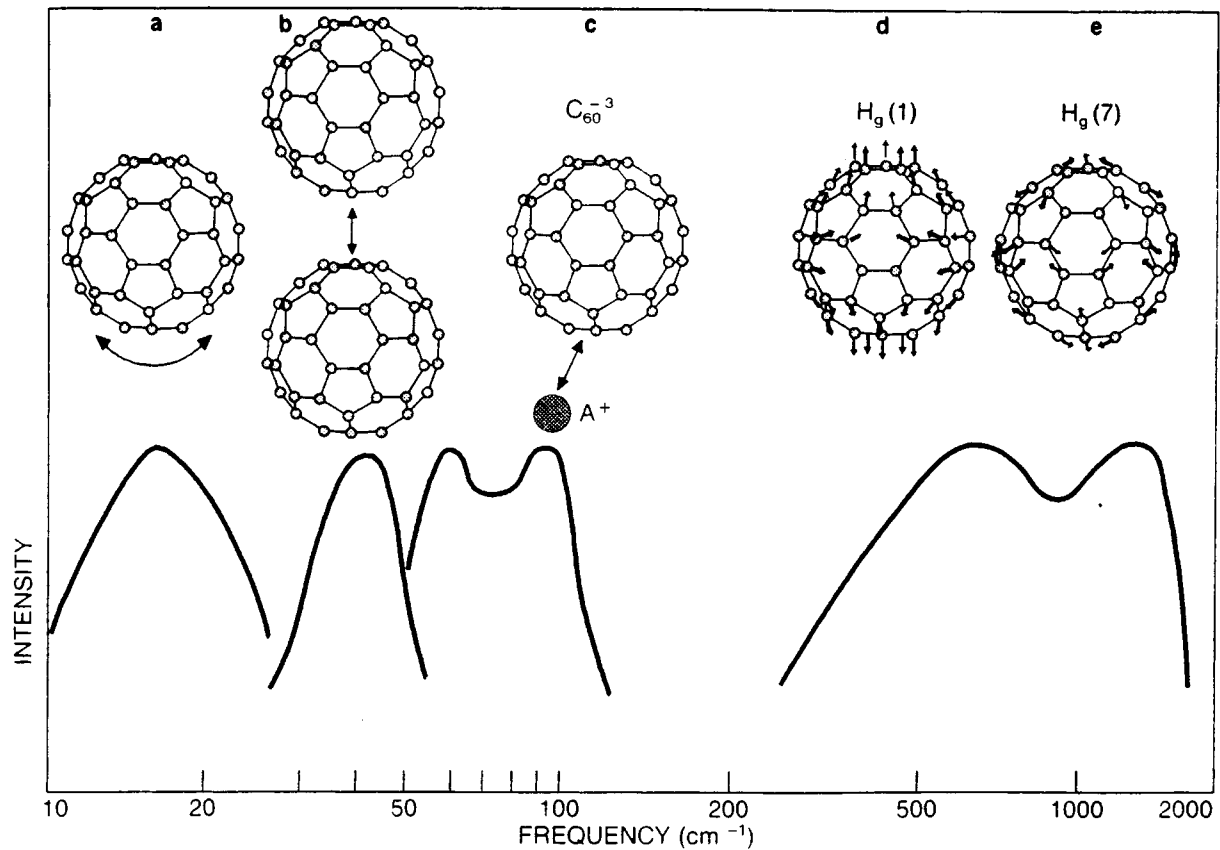


FIG. 6. Schematic representation of various phonons in A_3C_{60} compounds: (a) librations; (b) optic C_{60} — C_{60} phonons; (c) A — C_{60} phonons; (d),(e) intramolecular H_g modes. The figure indicates the radial and tangential character of the low-lying and high-lying H_g modes, respectively. After Hebard, (1992).

TABLE III. Phonon frequencies for the H_g and A_g modes. Different theoretical calculations are compared with experimental results for undoped solid C_{60} .

Mode	Varma ^a	Jishi ^b	Energy (cm^{-1})		Faulhaber ^c	Expt. ^f
			Antropov ^c	Quong ^d		
$H_g(8)$	1721	1575	1462	1576	1567	1575
$H_g(7)$	1596	1401	1387	1443	1425	1428
$H_g(6)$	1406	1217	1290	1244	1200	1250
$H_g(5)$	1260	1102	1091	1093	1067	1099
$H_g(4)$	924	788	785	767	750	774
$H_g(3)$	711	708	753	727	640	710
$H_g(2)$	447	439	454	439	421	437
$H_g(1)$	263	269	281	258	249	273
$A_g(2)$		1468	1463	1499	1493	1470
$A_g(1)$		492	458	478	459	496

^aVarma *et al.*, 1991.

^bJishi *et al.*, 1992.

^cAntropov, Gunnarsson, and Liechtenstein, 1993.

^dQuong *et al.*, 1993.

^eFaulhaber *et al.*, 1993.

^fBethune *et al.*, 1991.

2. Calculations of electron-phonon coupling

The electron-phonon coupling plays a crucial role in the theory of superconductivity. We introduce the dimensionless coupling to the phonon mode ν (Rainer, 1986)

$$\lambda_\nu = \frac{2}{N(0)} \sum_{\mathbf{q}} \frac{1}{\omega_{\nu\mathbf{q}}} \sum_{n,m,\mathbf{k}} |g_{n\mathbf{k},m(\mathbf{k}+\mathbf{q})}(\nu)|^2 \times \delta(\varepsilon_{n\mathbf{k}}) \delta(\varepsilon_{m(\mathbf{k}+\mathbf{q})} - \varepsilon_{n\mathbf{k}} - \omega_{\nu\mathbf{q}}), \quad (5)$$

where $N(0)$ is the electronic density of states per spin at the Fermi energy and $\omega_{\nu\mathbf{q}}$ is the energy of the ν th phonon with the wave vector \mathbf{q} . The energy of the n th electronic band with the wave vector \mathbf{k} is $\varepsilon_{n\mathbf{k}}$. Finally, $g_{n\mathbf{k},m(\mathbf{k}+\mathbf{q})}(\nu)$ is the matrix element between the two electronic states $n\mathbf{k}$ and $m(\mathbf{k}+\mathbf{q})$ of the potential created when a phonon $\nu\mathbf{q}$ is excited. Thus it follows that

$$g_{n\mathbf{k},m(\mathbf{k}+\mathbf{q})}(\nu) = \langle n\mathbf{k} | \Delta V_{\nu\mathbf{q}} | m(\mathbf{k}+\mathbf{q}) \rangle \frac{1}{\sqrt{2M\omega_{\nu\mathbf{q}}}}, \quad (6)$$

where $\Delta V_{\nu\mathbf{q}}$ is the induced potential per unit displacement along the phonon normal coordinate, $\sqrt{2M\omega_{\nu\mathbf{q}}}$ is the phonon amplitude, and M is the reduced mass.

The calculation of λ requires a double sum over a Brillouin zone of a quantity (g) which is very time consuming to calculate. In general, an accurate calculation of λ is therefore very complicated. For the intramolecular modes in the fullerides, important simplifications follow from the large difference between the intramolecular (E_I) and intermolecular (W) energy scales (Lannoo *et al.*, 1991). One can then assume that the phonon eigenvalues and eigenvectors are independent of \mathbf{q} . If in addition we assume that $W \ll E_I$ in the calculation of $g_{n\mathbf{k},m(\mathbf{k}+\mathbf{q})}(\nu)$ but keep the full structure of $|n\mathbf{k}\rangle$, the complicated Brillouin-zone sums can be performed analytically, and the problem is essentially reduced to a molecular problem (Lannoo *et al.*, 1991). The accuracy of these assumptions has been tested for a simple tight-binding model, where it was possible to perform the Brillouin-zone summations (Antropov, Gunnarsson, and Liechtenstein, 1993). It was found that the simplified calculation agreed fairly well with the full calculation, justifying the assumptions of Lannoo *et al.* (1991).

Thus it is sufficient to calculate the shift $\Delta\varepsilon_{\nu\alpha}$ of the t_{1u} level α for a free C_{60} molecule per unit displacement of the ν th phonon coordinate. One then finds that

$$\lambda \sim N(0) \sum_{\nu\alpha} \frac{\Delta\varepsilon_{\nu\alpha}^2}{\omega_\nu^2}. \quad (7)$$

This gives a molecular-specific quantity that must then be multiplied by the density of states $N(0)$, which is determined by the intermolecular hopping. The molecular calculation therefore gives a value for $\lambda_\nu/N(0)$, and it is appropriate to compare this quantity from different calculations. We observe that the quantity $\lambda_\nu/N(0)$ grows with the intramolecular energy scale, while $N(0)$ is inversely proportional to the intermolecular hopping. The large difference between these two energy scales

therefore favors a large value of λ (Schluter *et al.*, 1992a). It is also clear that, as the lattice parameter increases, the overlap between the C_{60} molecules is decreased, reducing the bandwidth. This leads to a larger density of states $N(0)$ and a larger λ , explaining the increase in T_c with lattice parameter (Fleming *et al.*, 1991; Rosseinsky *et al.*, 1991; Tanigaki *et al.*, 1993; Ramirez, 1994) (see also Fig. 3).

We notice that the results are quite sensitive to the phonon eigenvectors, and small changes in the eigenvectors can lead to large shifts of the coupling strength between different phonons. One can show, however, that $\sum_{\nu\alpha} (\Delta\varepsilon_{\nu\alpha})^2$ is independent of the phonon eigenvectors (Antropov, Gunnarsson, and Liechtenstein, 1993). A shift of coupling strength between phonons with similar energies therefore has a small effect on the total value of λ , while a shift between phonons of very different energies can dramatically change the total λ due to the energy denominator in Eq. (7). For instance, in the calculation of Antropov, Gunnarsson, and Liechtenstein (1993), mixing 5% of the weight ($\sqrt{0.05}$) of the seventh eigenvector into the eighth and vice versa changes the couplings 0.020 and 0.022 in Table IV to 0.010 and 0.030, i.e., a small change in the total coupling. The same mixing between the second and the eighth eigenvectors changes the couplings 0.006 and 0.022 to 0.033 and 0.019, i.e., a large change of the total coupling.

In Table IV we show some typical results of calculations of $\lambda/N(0)$. The calculation of Varma *et al.* (1991) was based on the semiempirical MNDO method. The calculation of Schluter *et al.* (1992b) used an empirical bond-charge model for the phonons and a LDA calculation for the electronic part. The work of Antropov, Gunnarsson, and Liechtenstein (1993) and Faulhaber *et al.* (1993) used *ab initio* LDA calculations both to generate the phonons and to calculate their interactions with the electrons. There are several other calculations. Mazin *et al.* (1992) performed an *ab initio* LDA calculation in the ASA-LMTO (Atomic Sphere Approximation-Linear Muffin Tin Orbital) formalism and used an empirical phonon model to obtain $\lambda/N(0) = 0.037$ eV. De Coulon *et al.* (1992) performed an *ab initio* LDA calculation using a pseudopotential Gaussian method and found $\lambda/N(0) \geq 0.04$ eV. Asai and Kawaguchi (1992) obtained $\lambda/N(0) = 0.070$ eV. The coupling to the $A_g(2)$ mode for a free molecule was estimated by Stollhoff (1991) to be $\lambda_{A_g(2)}/N(0) = 0.0025$ eV and by Scherrer and Stollhoff (1993) to be $\lambda_{A_g(2)}/N(0) = 0.01$ eV. Relatively small values for the coupling to the $A_g(2)$ mode were also deduced by Schluter *et al.* (1992a) [$\lambda_{A_g(2)}/N(0) = 0.005$ eV], Antropov, Gunnarsson, and Liechtenstein (1993) [$\lambda_{A_g(2)}/N(0) = 0.009$ eV], and Pickett *et al.* (1994) [$\lambda_{A_g(2)}/N(0) = 0.002$ eV].¹ These calculations do not include the screening effects discussed below. The

¹The values of λ quoted here differs from that given by Pickett *et al.* due to a different convention used by them.

TABLE IV. The partial electron-phonon coupling constants $\lambda_{\nu}/N(0)$ according to different theoretical calculations. The energies of the modes for the undoped system are shown.

Mode	Undoped energy (cm ⁻¹)	Varma ^a	$\lambda_{\nu}/N(0)$ (eV)		
			Schluter ^b	Antropov ^c	Faulhaber ^d
H _g (8)	1575	0.011	0.009	0.022	0.009
H _g (7)	1428	0.034	0.013	0.020	0.015
H _g (6)	1250	0.000	0.003	0.008	0.002
H _g (5)	1099	0.006	0.001	0.003	0.002
H _g (4)	774	0.000	0.007	0.003	0.010
H _g (3)	710	0.001	0.004	0.003	0.001
H _g (2)	437	0.001	0.007	0.006	0.010
H _g (1)	273	0.003	0.008	0.003	0.001
Σ H _g		0.056	0.052	0.068	0.049

^aVarma *et al.*, 1991.

^bSchluter *et al.*, 1992b.

^cAntropov, Gunnarsson, and Liechtenstein, 1993.

^dFaulhaber *et al.*, 1993.

electron-phonon interaction has also been calculated by Jishi and Dresselhaus (1992) and by G. Chen and Goddard (1993).

Table IV illustrates that there are substantial differences between the different calculations in terms of the distribution of coupling strength between the different modes. Thus Varma *et al.* (1991) found that almost all the coupling strength is in the two highest modes. Antropov, Gunnarsson, and Liechtenstein (1993) found more coupling strength in the lower phonon-modes, and this was still more true for the calculations of Schluter *et al.* (1992b) and Faulhaber *et al.* (1993). Nevertheless, all four calculations find the strongest coupling to one of the uppermost phonons. The large variation in the distribution of coupling between the different phonons in Table IV may to a substantial extent be due to the sensitivity to the phonon eigenvectors discussed below Eq. (7). These variations suggest that there are substantial uncertainties in the calculations.

In estimates of the total λ , the contributions from the A_g modes are usually not included. The reason is that the A_g contribution is expected to be screened out in A₃C₆₀ (A=K, Rb) (Schluter *et al.*, 1992b). This is illustrated by Raman-scattering results for A₃C₆₀ (A=K, Rb; Duclos *et al.*, 1991, Pichler *et al.*, 1992). As discussed in Sec. III.A.3, the additional broadening of the A_g modes in A₃C₆₀ compared with C₆₀ should be a measure of the electron-phonon coupling. Experiments, however, show little or no extra broadening of the A_g(2) in the metallic phase. For instance, Pichler *et al.* (1992) estimated the additional broadening to be only about 3 cm⁻¹, implying $\lambda_{A_g(2)}/N(0) \sim 0.0002$, i.e., an extremely small coupling. The corresponding additional broadening for many of the H_g modes is, on the other hand, large, indicating a much stronger coupling for these modes. The symmetric A_g mode leads to the same displacement of all the t_{1u} levels on a given molecule, and this displacement can largely be compensated by a transfer of charge to this molecule from other molecules. This screening is much

less efficient for the H_g modes, since they do not shift the center of gravity of the t_{1u} levels. Simple estimates within the random-phase approximation and assuming static screening suggest that the screening could reduce the coupling to the A_g mode by one to two orders of magnitude (Antropov, Gunnarsson, and Liechtenstein, 1993). It would be interesting to investigate nonadiabatic effects, which go beyond static screening, since the A_g(2) phonon energy is comparable to the energy scale of the screening.

To obtain values of λ , we also need estimates of the density of states at the Fermi energy $N(0)$. There have been several theoretical calculations of $N(0)$ for K₃C₆₀. A full-potential linear combination of Gaussian orbitals gave $N(0) = 6.6$ states/eV-spin for the so-called unidirectional structure, where all the C₆₀ molecules have the same orientation and there is one C₆₀ molecule per unit cell (Erwin and Pickett, 1991, 1992). An ASA-LMTO calculation gave $N(0) = 8.6$ states/eV-spin (Satpathy *et al.*, 1992), and a full-potential LMTO gave 7.0 states/eV-spin (Antropov, 1992). These and some other results are collected in Table V. A calculation for the bidirectional structure, where the molecules have two different directions, gave $N(0) = 7.5$ states/eV-spin (Antropov, 1992). The most relevant calculation, however, is probably for the orientationally disordered structure. This has only been performed within a tight-binding approach (Gelfand and Lu, 1992a, 1992b, 1993). In the disordered system the structures in $N(\epsilon)$ are smeared out and $N(0)$ may be reduced by 15–20%. Table V then suggests that $N(0) \sim 5$ –7 states/eV-spin for the disordered system.

Experimentally, the density of states has been estimated using a number of different techniques. Many estimates are based on the NMR relaxation rate. It has often been assumed that the Fermi contact interaction dominates the relaxation, and large values of $N(0)$ have been obtained. It has, however, been shown that the re-

TABLE V. The density of states $N(0)$ (per eV and spin) for K_3C_{60} and Rb_3C_{60} according to different band-structure calculations. Some of the results have been interpolated by Gelfand (1994).

$N(0)$ (K_3C_{60})	$N(0)$ (Rb_3C_{60})/ $N(0)$ (K_3C_{60})
6.6 ^a	1.26 ^a
7.0 ^b	
8.6 ^c	1.18 ^c
8.6 ^d	1.21 ^d
9.0 ^e	1.14 ^e
9.8 ^f	1.27 ^f

^aErwin and Pickett (1991, 1992).

^bAntropov (1992).

^cHuang *et al.* (1992).

^dSatpathy *et al.* (1992).

^eNovikov *et al.* (1992).

^fTroullier and Martins (1992).

laxation is dominated by the spin-dipolar interaction, due to the p_r character ($\sim 95\%$) of the states close to the Fermi energy (Antropov, Mazin, *et al.*, 1993). These results were supported by Tycko *et al.* (1993), who found that the spin-dipolar coupling dominates for RbC_{60} and CsC_{60} . Antropov, Mazin, *et al.* (1993) deduced that $N(0)=7.2$ and 8.1 states/eV-spin for K_3C_{60} and Rb_3C_{60} , respectively. These values are used in the following discussion.

$N(0)$ has also been estimated from the specific-heat jump ΔC at the superconducting transition (Ramirez, Kortan, *et al.*, 1992; Burkhart and Meingast, 1996). Using the formula

$$\frac{\Delta C}{T_c} \sim N(0)(1 + \lambda)(1.43 + O(\lambda^2)) \quad (8)$$

and $\lambda = 0.068N(0)$ (Antropov, Gunnarsson, and Liechtenstein, 1993), Burkhart and Meingast (1996) obtained $N(0)=6.6$ and 7.4 states/eV-spin for K_3C_{60} and Rb_3C_{60} , respectively. Using instead $\lambda = 0.147N(0)$ (Gunnarsson *et al.*, 1995), they found $N(0)=5.3$ and 5.9 states/eV-spin for K_3C_{60} and Rb_3C_{60} , respectively.

The density of states has furthermore been estimated from Pauli contribution to the susceptibility, obtained from superconducting quantum interference device (SQUID) and electron paramagnetic resonance (EPR) measurements, as is given in Table VI. The SQUID results were corrected for the diamagnetic contribution from the cores. The result of Wong *et al.* (1992) was also corrected for the Landau orbital diamagnetism, while Ramirez, Rosseinsky, *et al.* (1992) argued that this contribution is negligible in the present systems. The EPR measurements contain no diamagnetic contributions. The susceptibility may have an appreciable Stoner enhancement (Ramirez, Rosseinsky, *et al.*, 1992). Based on LDA calculations, this enhancement factor was estimated to be 1.34 and 1.42 for K_3C_{60} and Rb_3C_{60} , respectively (Antropov, Mazin, *et al.*, 1993). The accuracy of the LDA in this context is, however, not known. This Stoner enhancement has *not* been taken into account in Table VI, and the numbers in the table should be di-

TABLE VI. The density of states $N(0)$ (per eV and spin) for K_3C_{60} and Rb_3C_{60} as deduced from susceptibility measurements. The results have not been corrected for the Stoner enhancement, which would lead to reduced estimates of $N(0)$.

$N(0)$ (K_3C_{60})	$N(0)$ (Rb_3C_{60})/ $N(0)$ (K_3C_{60})	Method
14 ^a	1.36 ^a	SQUID
16 ^b		SQUID
11 ^b		EPR
15 ^c	1.40 ^d	EPR
10 ^d		EPR

^aRamirez, Rosseinsky, *et al.* (1992).

^bWong *et al.* (1992).

^cTanigaki *et al.* (1995).

^dD. Wang (1995).

vided by the appropriate Stoner enhancement. The susceptibility has recently been calculated for a threefold-degenerate Hubbard model, which describes the t_{1u} band and the on-site Coulomb interaction U . A quantum Monte Carlo lattice method was used to obtain the enhancement of the Pauli susceptibility due to the Coulomb interaction (Aryasetiawan *et al.*, 1997). For typical values of $U \sim 1.2-1.3$ eV, an enhancement of the order of a factor of 3 was obtained. This would reduce the values of $N(0)$ estimated from the susceptibility and roughly bring them in line with other estimates.

We remark that this discussion has not distinguished between the density of states and the density of quasi-particle states (Aryasetiawan *et al.*, 1997). We furthermore note that it is hard to estimate $N(0)$ from photo-emission or yield spectroscopy (De Seta and Evangelisti, 1995), due to a large broadening of the band, which is probably caused by phonon and plasmon satellites (Knupfer *et al.*, 1993) or other many-body effects. Various experimental estimates of $N(0)$ have been discussed by Gelfand (1994).

Table VII shows the contribution from the H_g modes to λ using the values of $N(0)$ deduced from NMR, i.e., $N(0)=7.2$ and 8.1 states/eV-spin for K_3C_{60} and Rb_3C_{60} , respectively.

It is interesting to compare the alkali fullerides with intercalated graphite, since the latter have much lower values (one to two orders of magnitude) of T_c than the fullerides. It has been reported that calculations for intercalated graphite give a substantially lower value (factor of 5) of λ than for the fullerides (Schluter *et al.*,

TABLE VII. The H_g contribution to λ according to different theoretical calculations, using $N(0)=7.2$ and 8.1 states (per eV and spin) for K_3C_{60} and Rb_3C_{60} , respectively.

Mode	Varma ^a	Schluter ^b	λ_ν Antropov ^c	Faulhaber ^d
K_3C_{60}	0.40	0.37	0.49	0.35
Rb_3C_{60}	0.45	0.42	0.55	0.40

^aVarma *et al.* (1991).

^bSchluter *et al.* (1992b).

^cAntropov, Gunnarsson, and Liechtenstein, (1993).

^dFaulhaber *et al.* (1993).

1992a). This is not ascribed to a larger density of states in the fullerenes but to the curvature of the C_{60} molecule (Benning *et al.*, 1991; Schluter *et al.*, 1992a, 1992b). In intercalated graphite, to first order there is no coupling to displacements perpendicular to the graphite planes. In C_{60} , on the other hand, the curvature mixes in $2s$ character in the primarily radial $2p$ orbital pointing out from the molecule, which dominates the states in the t_{1u} band. This allows for a coupling of these states to radial (transverse) modes. Alternatively, we can think of the displacements of the nuclei as setting up an approximately p -like perturbing potential close to the nuclei. Such a potential can couple a $2s$ and a $2p$ orbital but not two $2p$ orbitals on the same site. Pietronero and Strässler (1992) suggested as an alternative explanation that the violation of Migdal's theorem in A_3C_{60} may cause the large T_c in these compounds.

3. Raman and neutron scattering

Due to the electron-phonon coupling, a phonon can decay into an electron-hole pair of the appropriate energy. In the metallic fullerenes A_3C_{60} this decay channel is available and contributes to the width of the phonons. This width is therefore a measure of the electron-phonon coupling (Allen, 1972,² 1974), and for the ν th phonon it is given by

$$\gamma_\nu = \frac{2\pi\omega_\nu^2 N(0)\lambda_\nu}{g_\nu}, \quad (9)$$

where γ_ν is the full width at half maximum (FWHM), ω_ν is the phonon frequency, $N(0)$ is the density of states per spin, λ_ν is the electron-phonon coupling, and g_ν is the degeneracy of the phonon (5 for H_g). Due to the factor ω_ν^2 , the width of the high-lying phonons is often very large, and those phonons are hard to observe experimentally. The lowest order phonon self-energy for orientationally disordered A_3C_{60} has been calculated by Deshpande *et al.* (1994).

The width can be measured using Raman or neutron scattering. In an ordered system, Raman scattering samples the decay of a phonon for $\mathbf{q} \approx 0$, and it may be misleading for the decay in the rest of the Brillouin zone. In A_3C_{60} ($A=K, Rb$) there is, however, a strong orientational disorder (Stephens *et al.*, 1991), and Raman scattering should be relevant for the determination of the electron-phonon coupling integrated over \mathbf{q} (Schluter *et al.*, 1992c). The observed widths may therefore include some dispersion effects. These are, however, expected to be small for the intramolecular modes, due to the weak coupling between the molecules (Belosludov and Shpakov, 1992).

The widths of some of the H_g phonons were measured very early by Mitch *et al.* (1992a, 1992b). They performed Raman measurements for ultrathin films of alkali-doped A_xC_{60} compounds. Due to the small thickness of the film, they were able to dope the system con-

TABLE VIII. The partial electron-phonon coupling constants $\lambda_\nu/N(0)$ according to different experimental estimates. We also show the energies of the modes for the undoped system. (PES=photoemission electron spectroscopy.)

Mode	Undoped		$\lambda_\nu/N(0)$ (eV)		
	energy (cm ⁻¹)	Raman ^a	Neutron ^b	Raman ^c	PES ^d
$H_g(8)$	1575			0.002	0.023
$H_g(7)$	1428			0.003	0.017
$H_g(6)$	1250			0.001	0.005
$H_g(5)$	1099			0.001	0.012
$H_g(4)$	774		0.005	0.002	0.018
$H_g(3)$	710		0.001	0.002	0.013
$H_g(2)$	437	0.022	0.023	0.014	0.040
$H_g(1)$	273		0.014	0.034	0.019

^aMitch *et al.* (1992b).

^bPrassides *et al.* (1992).

^cWinter *et al.* (1996).

^dGunnarsson *et al.* (1995).

tinuously with Na, K, Rb, and Cs. For the $H_g(2)$ mode they observed a half-width of 14, 22, 22, and 20 cm⁻¹ for $A=Na$ $x=1$, $A=K$ $x=2.1$, $A=Rb$ $x=1.9$, and $A=Cs$ $x=2$, respectively. They assigned the rather x -independent broadening in NaC_{60} to disorder and assumed that the disorder is similar in the other compounds. The additional broadening in these compounds was assigned to the electron-phonon coupling. Assuming that the two mechanisms add quadratically, they deduced a width of 17 cm⁻¹ for the K and Rb doped C_{60} . To obtain a value for λ_2 from Eq. (9), one further has to assume a value for $N(0)$. Since different groups have used different values for $N(0)$, we use here $N(0)=7.2$ eV⁻¹ per spin, deduced from NMR for K_3C_{60} (Antropov, Mazin, *et al.*, 1993), to be able to compare the different estimates. The values quoted below therefore differ from the values of λ given in the original papers. In a few cases below we have also corrected for an incorrect prefactor in Eq. (9) that has appeared in the literature. In Table VIII we show different experimental estimates of $\lambda_\nu/N(0)$ for K_3C_{60} .

The phonon width has also been studied in neutron-scattering experiments for C_{60} , K_3C_{60} , and Rb_6C_{60} by Prassides *et al.* (1992). By comparing the broadening for the metallic K_3C_{60} and the insulating C_{60} , Prassides *et al.* deduced the additional broadening due to the electron-phonon coupling. This was performed for the four lowest H_g modes. The result for $H_g(2)$ is in good agreement with the result of Mitch *et al.* (1992b).

Recently, the Raman spectrum was studied by Winter and Kuzmany (1996) for single crystals and at low temperatures. They found that the peaks for several of the H_g phonons were strongly asymmetric and could be fitted with five components. This is shown in Fig. 7. It is interesting that the component with the largest shift relative to the position in the undoped crystal also has the largest width. This suggests that the different components have different electron-phonon couplings. The origin of such a difference in the coupling, if it exists, is, however, not clear. It is also interesting that the two

²Observe a misprint, which was corrected by Allen (1974).

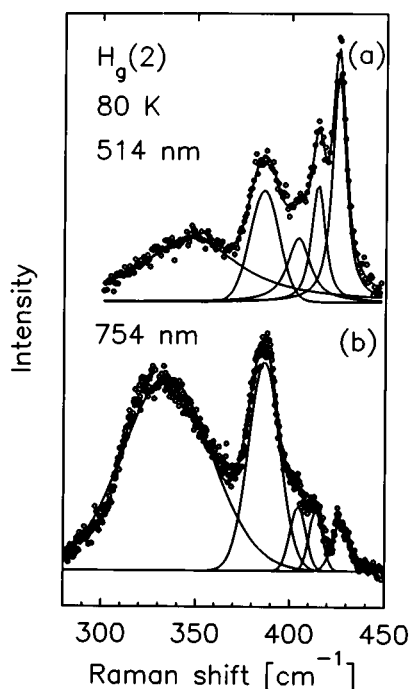


FIG. 7. Raman spectrum of the $H_g(2)$ mode: (a) excited with a green laser; (b) excited with a red laser. The full lines show a fit to five Voigtian profiles. After Winter and Kuzmany (1996).

highest H_g modes seemed to have a different pattern of splitting. The observed line shape therefore poses a very interesting theoretical problem. If it is assumed that the formula of Allen (1972, 1974) is still applicable to each component by itself, the results in Table VIII are obtained.

The measurement of the phonon broadening provides rather direct information about the electron-phonon coupling. We note, however, that the interpretation (Allen, 1972) is based on Migdal's theorem. Although this should be an excellent approximation for most systems, it is questionable for the fullerenes, since the phonon frequencies and the t_{1u} bandwidth are comparable (Pietronero and Strässler, 1992; Grimaldi *et al.*, 1995a, 1995b; Pietronero *et al.*, 1995). There is also a question of whether Jahn-Teller-like effects, studied for free molecules (Auerbach *et al.*, 1994; Manini *et al.*, 1994) and going beyond Migdal's theorem, could survive in the solid and influence the results. Such higher-order effects are very important for the photoemission spectrum of a free molecule discussed below. In particular, the interesting line shape obtained by Winter and Kuzmany (1996) raises questions about our understanding of how to analyze the spectra.

Reviews of Raman- and neutron-scattering studies of the fullerenes have been given by Kuzmany, Matus, *et al.* (1994) and by Pintschovius (1996), respectively.

4. Photoemission

An alternative way of deducing the electron-phonon coupling is the use of photoemission data. Because of

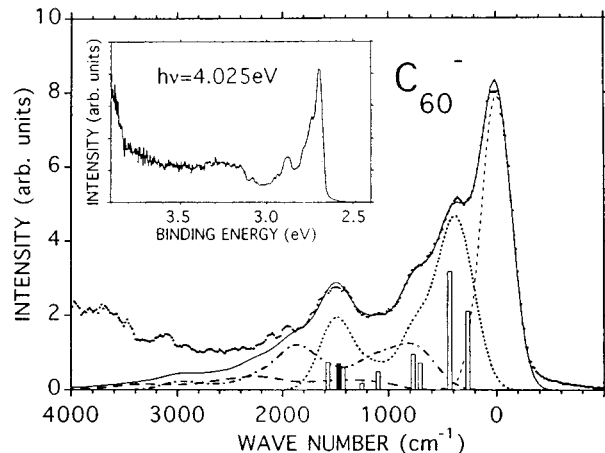


FIG. 8. The experimental (dots) and theoretical (solid line) photoemission spectrum of C_{60}^- . Dashed curve, theoretical no loss; dotted curve, single loss; dash-dotted curve, double loss. The contributions of the different modes to the single-loss curve are given by bars (H_g : open, A_g : solid). The inset shows the experimental spectrum over a larger energy range. After Gunnarsson *et al.* (1995).

the relatively strong electron-phonon coupling, we expect to see satellites due to the excitation of phonons. The weight of the satellites should then give information about the strength of the coupling. This is essentially the Franck-Condon effect, except that it is important to take the Jahn-Teller effect into account for C_{60} . The photoemission spectra of K_3C_{60} and Rb_3C_{60} have been analyzed along these lines (Knupfer *et al.*, 1993). Due to the broadening effects in a solid and to the complications in the theoretical treatment of bands with dispersion, however, it was not possible to derive reliable, quantitative values for the electron-phonon coupling.

Photoemission experiments have, however, been performed for free C_{60}^- molecules, for which the theoretical treatment is substantially simpler (Gunnarsson *et al.*, 1995). In these experiments a beam of C_{60}^- ions was created, and a photoemission experiment was performed using a laser light source ($\hbar\omega = 4.025$ eV) and a time-of-flight spectrometer. To analyze the results, a model was used that includes the t_{1u} level from which the electron is emitted, the two A_g and eight fivefold-degenerate H_g modes, and their coupling to the electronic state. For this model the ground state can be calculated to any desired accuracy by numerical diagonalization. Within the sudden approximation (Hedin and Lundqvist, 1969), the photoemission spectrum can furthermore easily be calculated. A set of coupling constants are then assumed, and the resulting spectrum is compared with experiment. The coupling parameters are then varied until good agreement with experiment is obtained, which thereby provides an estimate of the couplings. The resulting spectrum is compared with experiment in Fig. 8, and the corresponding parameters are shown in Table VIII.

This approach mainly contains three uncertainties. First, it is based on the sudden approximation. This ap-

proximation should become very accurate as the kinetic energy of the emitted electron becomes large. Due to the small photon energy used, to obtain a good resolution, the accuracy of the sudden approximation is unclear. Spectra taken at different photon energies did not, however, show any systematic variation, suggesting that the sudden approximation may not be a serious problem here. We further observe that the weight of the satellites must go to zero as the photon energy is reduced. If this happens in a monotonic way, the use of the sudden approximation would underestimate the couplings. As shown in Table VIII, the couplings derived from photoemission, however, tend to be larger than other estimates. The second uncertainty is more technical and is related to the fact that, for the resolution available, it is not possible to distinguish between the coupling to the A_g modes and the H_g modes with similar energies. The couplings to the A_g modes were therefore taken from a calculation by Antropov, Gunnarsson, and Liechtenstein (1993). With this assumption the couplings to the H_g modes can then be determined uniquely. An equally good fit to experiment could be obtained if, for instance, the coupling to the $A_g(2)$, $\lambda_{A_g(2)}/N(0)$, were allowed to vary between 0.00 and 0.03 eV, provided that the total coupling to the $H_g(7)$ and $H_g(8)$ modes were simultaneously varied between 0.07 and 0.00 eV. Thirdly, the coupling is determined for C_{60}^- , while we are interested in C_{60}^{3-} in a solid. Although the additional charging of C_{60} is not expected to have large effects, due to the sensitivity of the coupling to the phonon eigenvectors, the coupling could still be influenced.

5. Resistivity

The electric resistivity ρ can be caused by various scattering mechanisms. An important mechanism is often the electron-phonon interaction, in which electrons are scattered under the simultaneous excitation of phonons. Another mechanism is provided by electron-electron scattering. The contribution from both these mechanisms goes to zero as $T \rightarrow 0$. Deviations from periodicity, e.g., the orientational disorder, on the other hand, lead to an essentially temperature-independent resistivity. If the dominant contribution to the T -dependent part of the resistivity comes from the electron-phonon scattering, the resistivity provides an interesting check of the values of the electron-phonon coupling constants.

In Fig. 9 typical results for the temperature dependence are shown. For low T , it is found that the temperature-dependent part of $\rho(T)$ at constant pressure is approximately quadratic in T (Crespi *et al.*, 1992). This suggests that the mechanism at these values of T is electron-electron scattering (Palstra *et al.*, 1994). To obtain a reasonable magnitude, however, it is necessary to assume that the matrix element for electron-electron scattering is of the order 1 eV, that is, comparable to the t_{1u} bandwidth. Such a large matrix element would suggest a rather inefficient screening. The approximate T^2 behavior can, however, also be obtained

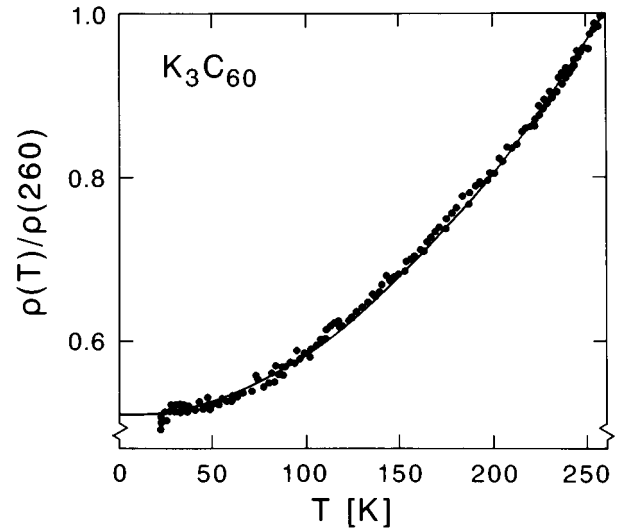


FIG. 9. T -dependent resistivity $\rho(T)$ normalized to the value at $T=260$ K: dotted curve, experimental (Xiang *et al.*, 1992); solid curve, theoretical.

from the electron-phonon mechanism with a reasonable distribution of coupling constants. Therefore we shall focus on this mechanism. More recent experimental work (Vareka and Zettl, 1994) has suggested that $\rho(T)$ at constant volume is linear in T down to relatively low T (100–200 K). This raises new questions, and the resistivity cannot be considered as fully understood.

The resistivity has been studied theoretically by several groups (Crespi *et al.*, 1992; Erwin and Pickett, 1992; Antropov, Gunnarsson, and Liechtenstein, 1993; Lannin and Mitch, 1994), using the theory of Ziman (Grimvall, 1981). This theory provides an approximate solution to the Boltzmann equation for the case of the electron-phonon scattering mechanism

$$\rho(T) = \frac{8\pi^2}{\omega_p^2 k_B T} \int_0^{\omega_{\max}} d\omega \frac{\hbar \omega \alpha_{tr}^2 F(\omega)}{\cosh(\hbar \omega / k_B T) - 1}, \quad (10)$$

where ω_p is the plasma frequency. In the following it is assumed that the transport coupling function $\alpha_{tr}^2 F(\omega)$ can be replaced by the electron-phonon coupling appropriate for superconductivity,

$$\alpha^2 F(\omega) = \frac{1}{2} \sum_{\nu} \omega_{\nu} \lambda_{\nu} \delta(\omega - \omega_{\nu}). \quad (11)$$

Due to the factor $\cosh(\hbar \omega / k_B T) - 1$ in the denominator of Eq. (10), it is clear that phonons with a frequency much larger than T do not contribute, but they give a linear contribution in T if their energy is much smaller than $k_B T$. Using this approach, Crespi *et al.* (1992) demonstrated that theoretical results for the coupling constants to the H_g modes alone, of the type obtained by Varma *et al.* (1991) or Schluter *et al.* (1992a, 1992b), gave a poor fit to experiment and a much too weak temperature dependence at small T . The reason is that the H_g phonons are too high in energy to give much contribution to $\rho(T)$ at low T , in particular since in these theories most of the coupling occurs to the

higher-energy phonons. The couplings of Jishi and Dresselhaus (1992), which emphasize the lower H_g phonons, gave better agreement. Crespi *et al.* (1992) argued that one also has to consider low-lying external modes, e.g., the intermolecular translational modes. Including such modes, they showed that the couplings of Varma *et al.* (1991), Schluter *et al.* (1992a, 1992b), and Jishi and Dresselhaus (1992) give reasonable descriptions of the experimental T dependence, if the coupling to the translational mode is chosen appropriately.

As an example of such results, we show a calculation using the coupling constants deduced from photoemission (Gunnarsson, 1995). In addition, the calculation included the coupling to the librations, using a theoretical coupling constant (Antropov, Gunnarsson, and Liechtenstein, *et al.*, 1993), and to the intermolecular modes, treating the coupling as an adjustable parameter, since its value is unknown. As in the calculation of Crespi *et al.* (1992), the energy of the intermolecular mode was set to 110 cm^{-1} , since neutron scattering shows many modes at this energy. We have set $\omega_p = 1.36 \text{ eV}$. It was further assumed that some other mechanism, e.g., orientational disorder, provides a T -independent resistivity that accounts for the resistivity just above T_c . The results are shown in Fig. 9. We can see that there is a good agreement with experiment over the whole temperature range. In particular, the approximate T^2 behavior is reproduced. This results from the contribution of many phonons at different energies, whose contributions to the resistivity are gradually switched on one after the other as T is increased. For high temperatures in Fig. 9, the resistivity corresponds to a mean free path of the order of, or less than, the separations between the molecules. This raises serious questions about the validity of the Boltzmann equation for these temperatures.

The theoretical and experimental results in Fig. 9 are for constant pressure. The experimental data have also been converted to constant volume by measuring the pressure dependence (Vareka and Zettl, 1994). The resistivity then shows an approximately linear behavior for temperatures larger than about 100 to 200 K. This linear behavior appears not to have been explained theoretically, and it is an interesting problem.

It is of particular interest to consider the absolute value of the resistivity increase with T , e.g., $\Delta\rho \equiv \rho(T=260) - \rho(T=0)$, since that may give information about the magnitude of λ . Many estimates of the resistivity, however, are made for low temperatures, thereby giving the residual resistivity and not $\Delta\rho$. Since the shape of $\rho(T)$, but not its absolute magnitude, appears to be very reproducible (Xiang *et al.*, 1992), we use the experimental ratio $\Delta\rho/\rho(T=0)$ to relate estimates of $\Delta\rho$ and $\rho(T=0)$. Here $\rho(T=0)$ refers to the resistivity just above the superconducting transition temperature. Thus we convert our theoretical estimate of $\Delta\rho$ to a theoretical estimate of $\rho(T=0) = 0.47 \text{ m}\Omega \text{ cm}$. It is interesting that the resistivity from orientational disorder, $0.32 \text{ m}\Omega \text{ cm}$ (Gelfand and Lu, 1992b, 1993), is not much smaller. Direct measurements for thin films and single crystals gave $\rho(T=0) \sim 1.2 \text{ m}\Omega \text{ cm}$ (Palstra *et al.*,

TABLE IX. The resistivity $\rho(0)$ in $\text{m}\Omega \text{ cm}$ just above the superconducting transition, according to different theoretical and experimental estimates. For details see text.

$\rho(0)$	Method
0.47	Theory. $\rho(260) - \rho(0) \rightarrow \rho(0)$
0.32 ^a	Theory. Disorder
1.2 ^b	Direct. Film
0.5 ^c	Direct. Single crystal
0.12 ^d	Paraconductivity
0.18 ^e	Upper critical field
0.77 ^f	Reflectivity. K—K
0.4 ^g	Reflectivity. S—N

^aGelfand and Lu (1992b, 1993).

^bPalstra *et al.* (1994).

^cHou *et al.* (1993).

^dXiang *et al.* (1993).

^eCrespi *et al.* (1992).

^fDegiorgi *et al.* (1992).

^gRotter *et al.* (1992).

1994) and $\rho(T=0) = 0.5 \text{ m}\Omega \text{ cm}$ (Hou *et al.*, 1993). Since the direct measurements involve various uncertainties (possibly somewhat granular structure for the thin films and geometrically very small samples for the single crystals), it is also interesting to compare them with indirect measurements of the resistivity. Xiang *et al.* (1993) deduced $\rho(T=0) = 0.12 \text{ m}\Omega \text{ cm}$ from the paraconductivity (additional conductivity due to superconducting fluctuations just above T_c), and Crespi *et al.* (1992) deduced $\rho(T=0) = 0.18 \text{ m}\Omega \text{ cm}$ from the upper critical field. Degiorgi *et al.* (1992) obtained $\rho(T=0) = 0.77 \text{ m}\Omega \text{ cm}$ from a Kramers-Kronig analysis of the reflectivity in the normal state, and Rotter *et al.* (1992) found $\rho(T=0) = 0.4 \text{ m}\Omega \text{ cm}$ from the ratio between the reflectivities in the normal and superconducting states. These results are summarized in Table IX.

Comparison between the theoretical and experimental estimates shows that the theoretical estimate falls in the correct range. Given the large range of experimental estimates, however, it is hard to assess the accuracy of the theoretical calculation. We also observe that the theoretical result was obtained from a set of coupling parameters that give very strong couplings to the low-lying modes, which leads to a large resistivity, while several other estimates of the couplings would give a substantially smaller resistivity.

The residual resistivity is smaller than the Mott limit, which, due to the small conduction-electron density, is rather large for these systems and has been estimated to be $1.4\text{--}2.0 \text{ m}\Omega \text{ cm}$ (Palstra *et al.*, 1994). For high temperatures, the resistivity corresponds to a mean free path shorter than the separation between the molecules. In such a situation the resistivity is usually expected to saturate at a maximum value (Fisk and Webb, 1976). Such a saturation is not observed for the doped C_{60} compounds up to rather high temperatures ($T \lesssim 500 \text{ K}$) (Hebard *et al.*, 1993), but for still larger temperatures it is seen in Rb_3C_{60} (Hou *et al.*, 1995). The saturation value

was estimated to be $\rho_{\text{sat}} = 6 \pm 3 \text{ m}\Omega \text{ cm}$, with the corresponding mean free path $l_{\text{sat}} = 1 \pm 0.5 \text{ \AA}$, significantly smaller than the separation between the molecules. The reason for this small mean free path does not appear to be understood, and it is an interesting question how one should conceptually understand such a short mean free path.

6. Comparison of electron-phonon coupling estimates

We are now in the position of comparing different theoretical (Table IV) and experimental (Table VIII) estimates of the coupling constants. We first of all observe that the quantity $\lambda/N(0)$ is obtained in the calculations and is deduced from photoemission, while Raman and neutron scattering gives an estimate of $\lambda N(0)$. Our assumptions about $N(0)$ (7.2 states/eV per spin for K_3C_{60}) is therefore crucial for these comparisons.

There are substantial differences between the different calculations of λ , between the different experimental estimates, and between theoretical and experimental values. Experimentally, a strong coupling to some of the low-lying modes is deduced. For instance, the total coupling to the lowest two modes is experimentally several times larger than the theoretical estimate. Thus the experimental estimates are 0.037, 0.048, and 0.059 eV, according to neutron, Raman, and photoemission experiments, respectively, while the theoretical estimates are 0.004, 0.015, 0.009, and 0.011 eV. For the high-lying phonons, the calculations give a rather strong coupling, in agreement with the results from photoemission but in contradiction with the results from Raman. It is not clear why there is such a large discrepancy between the photoemission and Raman results for these modes.

If a larger value for $N(0)$ is assumed, the discrepancy between the theoretical values and the Raman and neutron estimates for the low-lying modes would be reduced, but the discrepancy with the photoemission values would remain. At the same time the difference between the theoretical and the Raman estimates would be increased for the high-lying modes. As discussed above, relatively small errors in the phonon eigenvectors could lead to a large underestimate of the theoretical coupling to the low-energy modes.

B. Alkali phonons

Very early it was pointed out that the alkali modes may provide a strong electron-phonon coupling (Zhang, Ogata, and Rice, 1991). Each C_{60} molecule in A_3C_{60} is surrounded by 14 alkali atoms (6 octahedral and 8 tetrahedral). The corresponding phonon frequencies are low [0.013 eV (Prassides *et al.*, 1992), 0.014 eV (Renker *et al.*, 1993), 0.013 eV (Mitch and Lannin, 1993)], implying weak force constants. If an electron is transferred to a C_{60} molecule, one may then expect the surrounding alkali ions to move towards the C_{60} molecule, giving an efficient screening. It has been estimated that the alkali phonons could contribute an attractive interaction of the

order 0.9 eV (Zhang, Ogata, and Rice, 1991), which corresponds to $\lambda \sim 2$, i.e., a strong coupling. Later experiments demonstrated that T_c is approximately independent of the alkali-atom mass (see Secs. II.A and II.C), showing that the alkali modes must contribute very little to T_c . This was rationalized in terms of an efficient metallic screening (Gunnarsson and Zwicknagl, 1992). If an electron is transferred to a C_{60} molecule, there is a tendency to screen it by transferring charge from that molecule to more distant molecules. The alkali ions then couple essentially to the net charge change of the C_{60} molecule. Within the RPA this screening mechanism is very efficient, and when an electron is transferred to a C_{60} molecule the change of its net charge is only a few hundredths of an electron (Gunnarsson and Zwicknagl, 1992). The coupling to the alkali modes is then reduced by one to two orders of magnitude. Although the RPA may greatly overestimate the efficiency of the screening, this nevertheless suggests a large reduction of the coupling.

The alkali phonon frequency for the tetrahedral position has been calculated using the density-functional formalism in the local-density approximation by Bohnen *et al.* (1995). They found an energy of 0.015 eV, in good agreement with experiment.

C. Librations

Early point-contact measurements of the superconductivity gap gave a large value of $2\Delta/T_c$ (Z. Zhang *et al.*, 1991), suggesting strong-coupling effects and the coupling to low-energy modes. It was therefore suggested that the coupling to the librations may be of importance (Dolgov and Mazin, 1992; Mazin, Dolgov, *et al.*, 1993). There are several factors influencing this coupling. For the intramolecular phonons, the main changes in the matrix elements come from changes in bond lengths and bond angles, i.e., changes of the order of the intramolecular energy scale. For the librations, which involve rigid rotations of the molecules, only the hopping between the molecules is influenced, i.e., changes of the order of the intermolecular energy. The amplitude factor in Eq. (6) also tends to be small for the librations due to the large moment of inertia, $I_{ii} = 40MR^2$, where M is the carbon mass and R is the C_{60} radius. On the other hand, the very small libration frequency [$\sim 4 \text{ meV}$, (Christides *et al.*, 1992)] tends to increase both the amplitude factor in Eq. (6) and the λ in Eq. (5). It is therefore *a priori* not easy to estimate the magnitude of the coupling to the librations.

We observe that the simplifications in the calculation of the coupling to the intramolecular phonons (Lannoo *et al.*, 1991) do not apply to the librations, and the Brillouin-zone sums in Eq. (5) should be performed. This has been performed within a tight-binding formalism, which gave $\lambda_l/N(0) \sim 0.01$ (Antropov, Gunnarsson, and Liechtenstein, 1993). Comparing the splitting of the t_{1u} band at the Γ point in the tight-binding calculation and an ASA-LMTO local-density calculation suggests that λ_l should be reduced by about a factor of 10, which

gives $\lambda_l/N(0) \sim 0.001$ and $\lambda_l \sim 0.01$ (Antropov, Gunnarsson, and Liechtenstein, 1993). Thus the coupling to the librations is found to be very weak.

The coupling has also been studied experimentally by Christides *et al.* (1992) and Reznik *et al.* (1994). They studied the librations above and below T_c . Since the libration energy is smaller than the superconductivity gap 2Δ , the broadening of the libration due to the decay in electron-hole pairs should go to zero for small temperatures (Zeyher and Zwicky, 1990). Experimentally, however, no change in the width was observed when the temperature was lowered below T_c . It was therefore concluded that $\lambda_l < 0.08$, since a change in width should otherwise have been observed (Christides *et al.*, 1992).

D. Intermolecular modes

The lattice dynamics of K_3C_{60} has been studied by Belosludov and Shpakov (1992). They included the van der Waals interaction between the C_{60} molecules, the electrostatic interactions between the ions, Born-Mayer-type repulsive interactions to describe the repulsion of the ion cores, and a valence-force model to describe the covalent interaction between the carbon atoms inside a C_{60} molecule. The parameters were adjusted to reproduce the experimental intramolecular T_{1u} vibrations. This led to acoustic modes that at larger wave vectors were mixed with librational modes at about 3.5 meV. At larger energies (6 meV and 16 meV) they found bands of alkali and C_{60} character. This seems to be consistent with neutron-scattering experiments (Prassides *et al.*, 1991; Christides *et al.*, 1992). The translational phonons have also been studied by W. Zhang *et al.* (1992) for K_3C_{60} and by Y. Wang *et al.* (1991) for C_{60} .

Pickett *et al.* (1994) studied the electron-phonon coupling for translational modes. They used a tight-binding parametrization of the hopping integrals. A distortion of the lattice corresponding to the longitudinal zone-boundary (110) intermolecular optic mode was introduced. From the displacement of the band-structure energies Pickett *et al.* estimated that $\lambda \sim 0.01$ for these modes.³ The intermolecular modes should therefore have a small effect on T_c .

IV. COULOMB INTERACTION AND METALLICITY

In this section we discuss the Coulomb interaction between two electrons on a free C_{60} molecule (U_0) and for a molecule in the solid (U). The large Coulomb interaction has played an important role in the discussion about superconductivity in the fullerenes. This has ranged from the issue of why A_3C_{60} are not Mott-Hubbard insulators (Lof *et al.*, 1992), and whether or not retardation effects can reduce the Coulomb interaction enough to allow for superconductivity driven by the electron-phonon inter-

action (Anderson, 1991; Gunnarsson and Zwicky, 1992), to the suggestion that the Coulomb interaction could actually be the cause of superconductivity (Baskaran and Tosatti, 1991; Chakravarty *et al.*, 1991; Friedberg *et al.*, 1992).

A. Coulomb U_0 for a free molecule

A simple estimate of U_0 for a free molecule can be obtained by assuming that the charge from an electron is uniformly spread out over a sheet with radius R . The interaction between two electrons is then $e^2/R = 4.1$ eV, if $R = 3.5$ Å. This estimate neglects the relaxation of the charge density when an electron is added to the molecule. To include this, one has to perform self-consistent calculations for different numbers of electrons, a task which has been carried out by several groups. Most of these calculations were based on the local-density approximation of the density-functional formalism (Hohenberg and Kohn, 1964; Kohn and Sham, 1965; Jones and Gunnarsson, 1989). U_0 is given by the change of the position of the t_{1u} level when charge is added to this level. The calculated values were 3.0 (Pederson and Quong, 1992), 2.7 (Antropov *et al.*, 1992), 3.0 (de Coulon *et al.*, 1992), and 3.1 eV (Martin and Ritchie, 1993).

Estimates of U_0 can also be obtained from experimental data. One estimate is provided by

$$U_0 = I(C_{60}) - A(C_{60}) - E_g = 3.3 \text{ eV}, \quad (12)$$

where $I(C_{60}) = 7.6$ eV (de Vries *et al.*, 1992) is the ionization energy, $A(C_{60}) = 2.7$ eV (Hettich *et al.*, 1991) is the affinity energy, and $E_g = 1.6$ eV (Gensterblum *et al.*, 1991) is the band gap as measured by photoabsorption for a free C_{60} molecule. An alternative measure is given by

$$U_0 = I(C_{60}^-) - A(C_{60}^-) \sim 2.7 \text{ eV}, \quad (13)$$

where $I(C_{60}^-) = 2.7$ eV (Hettich *et al.*, 1991) is the ionization energy and $A(C_{60}^-)$ is the affinity energy of C_{60}^- . C_{60}^{2-} has been observed experimentally (Hettich *et al.*, 1991; Limbach *et al.*, 1991), and, if it is indeed stable, $A(C_{60}^-) > 0$ and $U_0 < 2.7$ eV. It may, however, be metastable with $A(C_{60}^-)$ slightly negative and U_0 slightly larger than 2.7 eV. The estimate of Eq. (12) refers to the interaction between a hole in the h_u level and an electron in the t_{1u} level, while the estimate of Eq. (13) refers to the interaction between two electrons added to a C_{60} molecule. Since the electron and hole try to stay together whereas the two electrons try to stay apart, it is not surprising that the latter estimate is smaller (Antropov *et al.*, 1992).

B. Coulomb U for the solid

In the solid, there are additional screening effects due to the polarization of the surrounding molecules when two electrons are added to a given molecule. In the following, we have a Hubbard model in mind, where the on-site Coulomb interaction is included, but the screening due to the polarization of the surrounding molecules is taken into account only implicitly, as a renormaliza-

³The value of λ quoted here differs from that given by Pickett *et al.* due to a different convention used by them.

tion of an effective U . The effect of this polarization has been calculated by putting polarizable molecules on a fcc lattice and allowing these molecules to polarize in a self-consistent way when charge is added to the central molecule. In this way the Coulomb interaction for a solid was found to be $U=1.27$ eV (Pederson and Quong, 1992) and 0.8–1.3 eV (Antropov *et al.*, 1992). For many purposes the Coulomb interaction may be drastically reduced by metallic screening. This reduction should, however, not be included if U is used in, say, a Hubbard model, since the metallic screening is then included explicitly in the model. To reduce the parameter U by the metallic screening would then involve double counting.

Experimentally, U has been estimated from Auger spectroscopy. Without any Coulomb interaction the Auger spectrum would be just a convolution of the one-particle spectrum, while the presence of an on-site molecular interaction U should displace the spectrum by approximately U . The comparison of the Auger spectrum with the convoluted photoemission spectrum then gives an estimate of $U=1.6$ eV (Lof *et al.*, 1992) and $U=1.4$ eV (Brühwiler *et al.*, 1992). For the highest occupied orbital (h_u) the estimate of U is about 0.2 eV smaller (Lof *et al.*, 1992), and for the t_{1u} orbital it may be somewhat smaller still. Due to surface effects, Auger spectroscopy may also slightly overestimate U (Antropov *et al.*, 1992).

C. Mott-Hubbard transition in systems with a large degeneracy

From the estimates of U and W it follows that the ratio U/W is substantially larger than one. It is then generally expected that the system will be a Mott-Hubbard insulator (Georges *et al.*, 1996). It has therefore been argued that stoichiometric A_3C_{60} must be an insulator and that the experimental samples of A_3C_{60} are metallic only because they are nonstoichiometric (Lof *et al.*, 1992). This would be similar to the situation for high- T_c superconductors, and it suggests that various properties of A_3C_{60} may be understood in a similar way. We therefore discuss the origin of the metallicity in A_3C_{60} in more detail.

The estimates of the critical value of U/W for a Mott-Hubbard transition have been made mostly for systems without orbital degeneracy, while the t_{1u} orbital has a threefold degeneracy. This was considered in early work of Lu (1994), who used the so-called Gutzwiller ansatz and approximation to find that the orbital degeneracy leads to a Mott-Hubbard transition for $U/W \sim (N+1)$, where N is the orbital degeneracy. This strong degeneracy dependence raised questions about its qualitative explanation and about why not almost all systems with partly filled bands are metals.

To discuss qualitatively the effect of orbital degeneracy, we consider a half-filled system with orbital degeneracy N and M sites. The band gap is given by

$$E_g = E(K+1) + E(K-1) - 2E(K), \quad (14)$$

where $K=NM$ is the number of electrons in the neutral state and $E(K)$ is the ground-state energy for K electrons. If we consider the system with K electrons in the limit of a large U , configurations with N electrons per site dominate the wave function. The hopping of an electron costs an energy U , and it is therefore strongly suppressed. In the state with $K+1$ electrons, the extra electron can, however, hop without an extra cost in Coulomb energy. In a simple Neel-like state, the extra occupancy can move through the hop of any of N electrons, which gives an extra factor \sqrt{N} in the corresponding hopping-matrix element compared with the one-electron case (Gunnarsson, Koch, and Martin, 1996). This suggests that the energy is lowered by about $\sqrt{N}\varepsilon_b$, where ε_b is the bottom of the one-particle band. Similar arguments for the $K-1$ electron state suggest that

$$E_g = U - \sqrt{N}W. \quad (15)$$

Exact diagonalization calculations and Monte Carlo calculations for A_3C_{60} (Gunnarsson, Koch, and Martin, 1996) support a \sqrt{N} dependence or a somewhat stronger degeneracy dependence and suggest that these results can be extrapolated to intermediate values of U . Detailed calculations led to the conclusion that the Mott-Hubbard transition takes place for $U/W \sim 2\frac{1}{2}$. This is at the upper limit of both experimental and theoretical estimates and suggests that A_3C_{60} is on the metallic side of a Mott-Hubbard transition. Although experimental samples of A_3C_{60} may be nonstoichiometric, there is no need to assume so in order to explain why they are metallic. These conclusions are strongly supported by experimental results of Yildirim, Barbedette, Fischer, Lin, *et al.* (1996). Since almost all physical systems have an orbital degeneracy, the degeneracy dependence of the Mott-Hubbard transition should be of interest for many other systems.

V. COULOMB PSEUDOPOTENTIAL

The electron-phonon interaction provides an attractive interaction between the electrons, which may be of the order of 1/10 eV. This interaction is counteracted by the Coulomb repulsion, which may lead to two electrons on the same molecule in an undoped C_{60} solid feeling a repulsion of the order $U \sim 1-1\frac{1}{2}$ eV (see Sec. IV.B). In this section we first discuss how the Coulomb repulsion may be reduced by screening and retardation effects. A dimensionless quantity

$$\mu = UN(0) \quad (16)$$

is introduced, in which U is some typical (screened) interaction and $N(0)$ is the density of states per spin. Due to retardation and other effects, μ is renormalized to μ^* , the Coulomb pseudopotential. A closely related issue is the question of whether the Coulomb interaction could be so effectively reduced that it becomes attractive, providing an electronic mechanism for superconductivity. This goes back to calculations for a model of a free molecule by Chakravarty *et al.* (1991) and is discussed in the last part of this section.

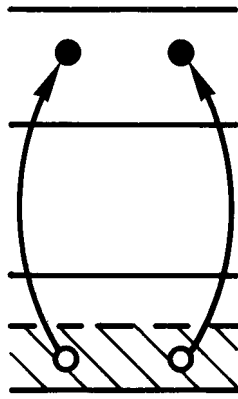


FIG. 10. Schematic picture of two sub-bands and the virtual Coulomb scattering of two electrons into the higher sub-band.

A. Retardation effects: Summing ladder diagrams

It was very early pointed out that the Coulomb repulsion can be reduced by retardation effects (Bogoliubov *et al.*, 1958; Morel and Anderson, 1962; Schrieffer, 1964; Ginzburg and Kirzhnits, 1982). Normally, the electronic energy scale is much larger than the energy scale of the phonons. By undergoing multiple scattering into higher-energy states, the electrons can move in a correlated way that reduces the Coulomb interaction but still has an attractive interaction via the phonons. This is shown schematically in Fig. 10 for scattering into a higher sub-band. Mathematically, this is usually expressed by summing ladder diagrams (see Fig. 11). In simple models, e.g., assuming that all Coulomb matrix elements are equal, the ladder diagrams can be summed, giving the effective interaction (Bogoliubov *et al.*, 1958; Morel and Anderson, 1962; Schrieffer, 1964; Ginzburg and Kirzhnits, 1982)

$$\mu^* = \frac{\mu}{1 + \mu \ln(B/\omega_{ph})}, \tag{17}$$

where B is a typical electron energy (half the bandwidth) and ω_{ph} is a typical phonon energy. If $B/\omega_{ph} \gg 1$, μ^* can be strongly reduced relative to μ . In the limit $\mu \ln(B/\omega_{ph}) \gg 1$, Eq. (17) simplifies to $\mu^* \approx 1/\ln(B/\omega_{ph})$, which may be of the order of 0.1–0.2. The importance of this reduction is illustrated by the McMillan formula (McMillan, 1968) for the transition temperature,

$$T_c = \frac{\omega_{ln}}{1.2} \exp\left[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right]. \tag{18}$$

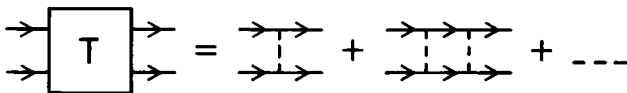


FIG. 11. Ladder diagrams describing the repeated scattering of two electrons. A solid line represents an electron and a dashed line the (screened) Coulomb interaction.

In this formula, the relevant quantity is

$$\frac{\lambda}{(1+\lambda)} - \mu^* \frac{1+0.62\lambda}{1+\lambda} \approx \frac{\lambda}{(1+\lambda)} - \mu^*. \tag{19}$$

It is immediately clear that μ^* is as important as λ in determining T_c .

Doped C_{60} compounds have a number of narrow subbands with a width of about 1/2 eV spread out over about 30 eV (see Fig. 2). It has been argued that the relevant energy scale is the total width of all the subbands (Varma *et al.*, 1991). Using Eq. (17) one then finds that $\mu^* \sim 0.2$ is only slightly larger than what is believed to be the case for conventional superconductors. Together with current estimates of λ , values of T_c of the right order of magnitude can then easily be obtained (Varma *et al.*, 1991; Mazin *et al.*, 1992; Schluter *et al.*, 1992a; 1992b). On the other hand, Anderson (1991) asserted that the relevant energy scale is the width of the t_{1u} subband. Since this energy is comparable to the phonon energies, the retardation effects are then expected to be small. Anderson therefore argued that μ^* is large and that the phonon mechanism alone cannot explain the superconductivity.

We first discuss the retardation effects on μ^* within the formalism described above, where ladder diagrams in the screened Coulomb interaction are summed. Later we discuss effects beyond this formalism. A crucial quantity is the Coulomb matrix element for scattering two electrons from the t_{1u} band into higher subbands (see Fig. 10). If these matrix elements are very small, the higher subbands should play a small role in this formalism. Chakravarty, Khlebnikov, and Kivelson (1992) analyzed this in a model that included the on-site interaction U_C between two electrons on the same carbon atom and the interaction V_C between two electrons on different carbon atoms on the same C_{60} molecule. They found that the Coulomb-scattering matrix element between different subbands is of the order of $U_C/60$, while the interaction within the same band is $U_C/60 + V_C$. Assuming that $U_C \approx 5-10$ eV and $V_C \approx 0.5-1.0$ eV, they found that the interband interaction is very much smaller than the intraband interaction.

The matrix elements of the screened Coulomb interaction have been studied in the random-phase approximation (RPA) (Gunnarsson and Zwicknagl, 1992; Gunnarsson *et al.*, 1992). The system was described in a tight-binding approach (Satpathy *et al.*, 1992; Laouini *et al.*, 1995) with one $2s$ and three $2p$ orbitals per carbon atom, and the screening was calculated with local-field effects included. A long-range Coulomb interaction was included, which involved an interaction between different atoms both on the same C_{60} molecule and on different molecules. The Coulomb interaction on a carbon atom was set to $U_C = 12$ eV. A screening calculation within the LDA was performed by D.P. Joubert (1993) with fairly similar results. The tight-binding results are shown in Table X. The table shows both intraband and interband interactions

TABLE X. The intraband Coulomb interactions [Eq. (20)] between two equal $W(\alpha\alpha, \alpha\alpha, \mathbf{q})$ and two different $W(\alpha\alpha, \beta\beta, \mathbf{q})$ t_{1u} conduction-band Bloch states as well as the largest interband scattering matrix element $W^{\text{inter}}(t_{1u} \rightarrow t_{1g})$. We consider both a free molecule (Mol) and a solid (Sol), where in the latter case $\mathbf{q} = \mathbf{G}/2$ and $\mathbf{q} = \mathbf{G}/20$, where $\mathbf{G} = 2\pi/a(1,1,1)$.

	Sys	$W(\alpha\alpha, \alpha\alpha, \mathbf{q})$		$W(\alpha\alpha, \beta\beta, \mathbf{q})$		W^{inter}	
		$\mathbf{G}/20$	$\mathbf{G}/2$	$\mathbf{G}/20$	$\mathbf{G}/2$	$\mathbf{G}/20$	$\mathbf{G}/2$
Unscreened	Mol		3.81		3.63		0.77
Screened	Mol		3.72		3.67		0.14
Unscreened	Sol	176.8	2.03	176.7	1.86	1.01	0.98
Undoped	Sol	78.9	1.68	78.8	1.63	0.15	0.15
Doped	Sol	0.094	0.065	0.060	0.031	0.10	0.10

$$W(\alpha\beta, \gamma\delta, \mathbf{q}) = N \int d^3r d^3r' \psi_{\alpha\mathbf{k}}^*(\mathbf{r}) \psi_{\beta\mathbf{k}+\mathbf{q}}(\mathbf{r}) \times W(\mathbf{r}, \mathbf{r}') \psi_{\gamma\mathbf{k}}(\mathbf{r}') \psi_{\delta\mathbf{k}+\mathbf{q}}^*(\mathbf{r}'), \quad (20)$$

where

$$\psi_{\alpha\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\nu} e^{i\mathbf{k}\cdot\mathbf{R}_{\nu}} \varphi_{\alpha}(\mathbf{r} - \mathbf{R}_{\nu}) \quad (21)$$

is a Bloch sum of molecular orbitals $\varphi_{\alpha}(\mathbf{r})$, $W(\mathbf{r}, \mathbf{r}')$ is the screened interaction, and N is the number of unit cells. The intraband integrals correspond to the interaction of charges that integrate to one in the unit cell, i.e., these integrals are dominated by a monopole interaction. On the other hand, $\phi_{\alpha}(\mathbf{r})\phi_{\beta}(\mathbf{r})$ with $\alpha \neq \beta$ integrates to zero, and therefore the interband matrix elements $W(\alpha\beta, \alpha\beta)$ correspond to multipole interactions. In the solid and without screening, the intraband matrix elements are therefore very large for small \mathbf{q} , since they represent the interaction of monopoles placed on the different molecules and with slowly varying phase factors. When screening is introduced in the undoped solid, these integrals are reduced due to the polarization of the molecules. This reduction is much more dramatic in the doped solid due to the effective metallic screening, which involves a charge transfer between the molecules. The unscreened interband matrix elements are much smaller than the unscreened intraband elements, due to the shorter range of the multipole interaction. In the undoped solid they are further reduced, primarily due to rearrangement of the charge density inside the molecule. In the doped solid, the metallic screening does not further reduce these matrix elements very much, since a charge transfer between the molecules does not contribute to the screening of multipoles. The moderate reduction shown in Table X is due to the change in the filling of the levels and the new channels (in particular, $t_{1u} \rightarrow t_{1g}$) opened up for intramolecular screening. It has been argued that the intraband (metallic) screening should not be included in the calculation of the interband matrix elements (Lammert *et al.*, 1995). The calculations discussed above show, however, that the metallic screening of the interband matrix elements is negligible (Gunnarsson *et al.*, 1992).

The Coulomb integral $W(\alpha\beta, \alpha\beta)$, with $\alpha \neq \beta$ referring to the t_{1u} orbitals, is also of great interest, since it

may tend to favor singlet states (Lammert and Rokhsar, 1993). With only the short-range on-site carbon interaction U_C , it is $U_C/100 = 0.12$ eV for a free molecule (Lammert and Rokhsar, 1993). Inclusion of the long-range Coulomb interaction reduces the integral to 0.09 eV, implying that the long range of the Coulomb interaction is not very important for this integral [in contrast to the monopole integral $W(\alpha\alpha, \alpha\alpha)$]. When screening is taken into account, $W(\alpha\beta, \alpha\beta)$ is reduced to 0.023 eV. This value is essentially unchanged if the screening by the surrounding molecules is included.

Because of the very efficient metallic screening of the intraband matrix elements, at least within the RPA, these matrix elements are smaller than the largest interband matrix elements. These results depend crucially on the fact that these matrix elements have very different character (monopole versus multipole interaction). This behavior is also very different from that of the electron gas, since there is an abrupt change in character when going from one subband to another, even if they are close in energy, due to the fact that each subband is derived from a different molecular level with a different spatial character. Since Eq. (17) is derived under the assumption that all matrix elements are equal, it cannot be used here. Approximate summing of the ladder diagrams, using the calculated matrix elements, shows that μ^* is close to zero in this formalism (Gunnarsson and Zwicknagl, 1992).

It is interesting to ask why the intraband matrix elements are so small. The screened interaction can be written as

$$W = (1 - vP)^{-1}v, \quad (22)$$

where W is a matrix representing the different Coulomb matrix elements, v is the corresponding unscreened matrix elements, and P is the polarizability, which is here calculated in the RPA. For the intraband matrix elements, the t_{1u} orbitals dominate the screening, and we can transform to the corresponding basis and neglect all other orbitals. For small $|\mathbf{q}|$, the diagonal elements of P are then related to the density of states $N(0)$ per spin. Since both $N(0)$ and the diagonal elements of v are large, we can assume that the product is much larger than unity. Essentially, the two factors v in Eq. (22) drop out, and with appropriate assumptions one can

then derive (Gunnarsson, Rainer, and Zwicknagl, 1992) that the intraband matrix elements are

$$\frac{1}{3}W(\alpha\alpha, \alpha\alpha, \mathbf{q}) + \frac{2}{3}W(\alpha\alpha, \beta\beta, \mathbf{q}) \approx \frac{1}{2N(0)} \quad (23)$$

for small $|\mathbf{q}|$. To obtain the unrenormalized μ we multiply by $N(0)$, obtaining $\mu \approx 0.5$. Averaging over q gives $\mu \approx 0.4$. We note that W becomes very small in the RPA for large $N(0)$, since in the RPA the cost of screening is purely a kinetic-energy cost and for a large $N(0)$ this cost is very small. For large values of U , we expect the RPA to become a poor approximation, and it is therefore interesting and important to know how accurate the RPA is in this case.

B. Retardation effects: Beyond ladder diagrams

The retardation effects considered above were all within a framework in which ladder diagrams in the screened interaction were summed. This raises the question of how valid it is to neglect other diagrams. For instance, Grabowski and Sham (1984) studied the lowest-order vertex corrections for the electron gas and found important corrections. Gunnarsson, Rainer, and Zwicknagl (1992) constructed other sets of diagrams, which to a large extent canceled the ladder diagrams. This raises important questions about which diagrams to include.

To circumvent this problem, Gunnarsson and Zwicknagl (1992) and Gunnarsson, Rainer, and Zwicknagl (1992) studied a two-band model in which some exact results can be obtained. They considered the Hamiltonian

$$\begin{aligned} H = & \sum_i \sum_{v=1}^2 \sum_{\sigma} \varepsilon_v n_{iv\sigma} + t \sum_{\langle ij \rangle} \sum_{v=1}^2 \sum_{\sigma} \psi_{iv\sigma}^{\dagger} \psi_{jv\sigma} \\ & + U_{11} \sum_i \sum_{vv'\sigma\sigma'} n_{iv\sigma} n_{iv'\sigma'} \\ & + U_{12} \sum_i [\psi_{i2\uparrow}^{\dagger} \psi_{i2\downarrow}^{\dagger} \psi_{i1\downarrow} \psi_{i1\uparrow} + \text{H.c.}], \end{aligned} \quad (24)$$

where n is an occupation number operator, i is a site index, ε_v are the energies of the two levels, t is the hopping integral, U_{11} is the intraband interaction, U_{12} is the interband scattering, and H.c. denotes a Hermitian conjugate. The particularly strong interband scattering between the t_{1u} and t_{1g} bands in C_{60} is of a similar type, namely the excitation of two electrons between two bands (see Fig. 10). Gunnarsson *et al.* assumed that

$$\Delta\varepsilon \equiv \varepsilon_2 - \varepsilon_1 \gg U_{12}, t. \quad (25)$$

In this limit, the upper subband can be projected out, and a new effective Hamiltonian can be obtained which describes low-energy properties correctly. This process does not generate any new terms for the Hamiltonian (24), but it renormalizes the intraband interaction to

$$U_{\text{eff}} = U_{11} - \frac{U_{12}^2}{2\Delta\varepsilon}. \quad (26)$$

If it is now assumed that $U_{12}^2/(2\Delta\varepsilon) \ll U_{11}$, the renormalization of the intraband interaction is small. The properties of this effective Hamiltonian then differ very little from the one-band model, in which the upper band was completely neglected. Thus the upper band has a small influence on the low-energy properties in general and μ^* in particular. For instance, in the RPA the screened interaction is $1/[2N(0)]$ in both the one-band and the two-band model, if $U_{11}N(0) \gg 1$.

On the other hand, the ladder diagrams in the screened interaction due to scattering into the upper subband can be summed. If it is assumed that

$$\frac{1}{N(0)} \lesssim \frac{U_{12}^2}{2\Delta\varepsilon}, \quad (27)$$

this approach predicts a large renormalization of μ^* . The ladder diagrams subtract a quantity $U_{12}^2/(2\Delta\varepsilon)$, which, although small compared with U_{11} , is large compared with the screened interaction in the limit considered. Thus the summation of ladder diagrams leads to a qualitatively incorrect result in this case.

The projection method and the summation of ladder diagrams describe similar physics. The difference is that in the rigorous projection method the high-energy degrees of freedom were eliminated first, while in the ladder-diagram approach the low-energy degrees of freedom were treated first (by introducing the metallic screening) and the high-energy degrees of freedom later (by summing the ladder diagrams). These results should be of relevance for the retardation effects due to high-lying states for conventional superconductors as well.

The model above contains important features of A_3C_{60} , and the assumptions are not too unrealistic for this system. The results therefore suggest that the summation of ladder diagrams in the screened interaction gives unreliable results for A_3C_{60} and that the renormalization of μ^* due to the higher subbands may not be large. Consequently, for simplicity one may assume that this renormalization can be neglected completely. If in addition RPA screening is used, one arrives at $\mu^* \sim 0.4$. The approach above has addressed only the renormalization due to the higher subbands and not that due to processes within the t_{1u} band itself. If we assume that the traditional theory is valid for these processes, μ^* is renormalized to 0.3 according to Eq. (17), if we set $B = 0.25$ eV and $\omega_{\text{ph}} = 0.1$ eV. This value can then be used in the McMillan formula, whereas $\mu^* = 0.4$ applies to the Eliashberg equation including one subband. We notice that only static screening was considered above, and inclusion of dynamic effects may influence the results substantially (Rietschel and Sham, 1983).

Takada (1993) considered a model that included electrons in the t_{1u} band, phonons, and plasmons, in which the plasmons screened the strong Coulomb repulsion. Guided by the Ward (1950) identity and work by Nambu (1960), Takada used an approximate vertex correction. In this way he was able to include corrections to Migdal's theorem, vertex corrections to the electron-electron scattering in the t_{1u} band, and the dynamical

screening of the Coulomb interaction. He found that the corrections to Migdal's theorem enhanced the value of T_c for moderate values of the phonon frequency. Furthermore, the vertex corrections to the electron-electron scattering reduced T_c . Thus Takada found a partial cancellation of the enhancement (Rietschel and Sham, 1983) of T_c due to dynamic screening effects, as had also been found by (Grabowski and Sham, 1984). Takada used the value $\mu=0.4$ for the Coulomb pseudopotential derived above to describe static screening effects and the renormalization due to scattering in other subbands than the t_{1u} band. Using $\lambda=0.58$ and adjusting the electron-plasmon coupling, he could then reproduce the experimental T_c for K_3C_{60} . The corresponding isotope effect, $\alpha=0.15$ for K_3C_{60} , was, however, surprisingly small. To describe the lattice-parameter dependence of T_c , Takada had to assume that $\mu=0.4W_0/W$, where W_0 and W are the bandwidths of K_3C_{60} and the system studied, respectively. This is somewhat surprising, since in the RPA μ is predicted to be essentially independent of the lattice parameter.

C. Electronic mechanisms

Chakravarty and Kivelson (1991), Chakravarty *et al.* (1991), and Baskaran and Tosatti (1991) proposed that there may be an effective attractive interaction between the electrons in a C_{60} molecule of a purely electronic origin. Chakravarty and Kivelson (1991) introduced a Hubbard model of the π -electron system in a free molecule with an on-site interaction U_C only. Using second-order perturbation theory, they calculated the energy of C_{60} , C_{60}^- , and C_{60}^{2-} . This provided an estimate of the effective repulsion for C_{60}^- . When the singlet state of C_{60}^{2-} was considered, the result consisted of a positive, linear term and a negative, quadratic term in U_C . The interaction therefore becomes attractive for sufficiently large $U_C \sim 3t_0$, where t_0 is the intramolecular hopping. The tendency to form a singlet state results from an integral of the type $W(\alpha\beta, \alpha\beta)$ [see Eq. (20)] with $\alpha \neq \beta$ belonging to the t_{1u} band (Lammert and Rokhsar, 1993), which may become negative when the higher states are projected out in second-order perturbation theory. The following discussion has focused on the validity of the second-order perturbation theory and the neglect of a long-range Coulomb interaction in this type of work.

White *et al.* (1992) addressed the question of the validity of second-order perturbation theory by studying small model systems. In particular, they considered a model with twelve atoms located on a truncated tetrahedron. For this system exact diagonalization can be performed and compared with second-order perturbation theory. White *et al.* (1992) concluded that second-order perturbation theory is qualitatively correct for intermediate values of U_C in the sense that exact diagonalization also gives an attractive interaction, but second-order perturbation theory may greatly overestimate the magnitude. Auerbach and Murthy (1992) and Murthy and Auerbach (1992) studied a model with electrons on a sphere and an interaction of variable range. They cal-

culated the second-order contribution to pairing and estimated the third-order terms. The second- and third-order contributions were found to be comparable at an interaction strength substantially smaller than the strength that leads to pairing in the second-order calculation. This again raises doubts about the accuracy of the second-order calculation. Berdenis and Murthy (1995) performed a renormalization-group calculation for a Hubbard model of C_{60} using a method of Tokuyasu *et al.* (1993). This method remains accurate up to larger values of the atomic U_C than the second-order perturbation theory, but its accuracy becomes questionable at roughly the value of U_C where it predicts an attractive interaction. Thus it still seems to be unclear whether or not the interaction can be attractive for an on-site Hubbard model of a free C_{60} molecule.

Goff and Phillips (1992, 1993) and Auerbach and Murthy (1992) have studied the effective interaction as a function of the range of the interaction. They found that the use of a more long-ranged interaction tended to suppress the formation of an attractive effective interaction. With an on-site interaction, two electrons added to the t_{1u} orbitals can almost avoid being on the same site simultaneously, and they have only a weak direct interaction $W(\alpha\alpha, \alpha\alpha)$. It is then not entirely surprising that the renormalized interaction $W(\alpha\beta, \alpha\beta)$ can lead to an effective attractive interaction. If the interaction becomes more long ranged, the direct interaction rapidly increases, leading to a repulsive effective interaction. For the free molecule, the interaction is long range, and there is actually an "antiscreening" effect for electrons on the opposite side of the molecule (Gunnarsson, Rainer, and Zwicky, 1992). The reason is that, for a finite system, screening charge cannot be moved to infinity as for an infinite system. It is therefore no surprise that the effective interaction for the free molecule is large and repulsive, as discussed in Sec. IV.A. Chakravarty, Gelfand, and Kivelson (1991) therefore from the start pointed out that the attractive electronic mechanism could become operative only if the screening inside the molecule were much more efficient in the metal than in the free molecule.

Lammert *et al.* (1995) considered a model with a long-range Coulomb interaction. They argued that the molecules surrounding a specific molecule provide a metallic environment, which they approximated by a metal with a spherical cavity with radius R_c . In this way the corresponding degrees of freedom were integrated out first, although the metallic screening corresponds to a low energy scale in the problem [$W \sim \omega_{pl} \sim 0.5$ eV (Knupfer *et al.*, 1995)]. The resulting screened interaction was calculated and used for the low-frequency interactions in the problem. The effective singlet two-body interaction was then calculated diagrammatically, including the first- and second-order diagrams. An attractive interaction was obtained for R_c in the range 5–6 Å and for an on-site atomic U_C in the range 8–10 eV.

An alternative way of treating the problem within this spirit is to express the metallically screened interaction $U_{\text{met,scr.}}$ in terms of the Coulomb interaction U_0 between

two electrons on a free C_{60} molecule. It is first assumed that in the solid the addition of a charge q to a molecule induces a potential $-qV_0$ due to the metallic screening by the surrounding molecules, reducing U_0 to

$$U_{\text{met.scr.}} = U_0 - V_0 \quad (28)$$

in the solid. We assume here that, due to the small hopping between the C_{60} molecules, the surrounding molecules respond to a spherically symmetric average of the charge on the central molecule. The model of Lammert *et al.* (1995) replaces the surrounding by a spherical cavity with $V_0 = e^2/R_c$. To obtain an estimate of V_0 (or R_c) in the above spirit, one can treat the surrounding C_{60} molecules as grounded, metallic spheres with radius 4.46 \AA (which reproduces the experimental molecular polarizability). This leads to $V_0 = 2.2 \text{ eV}$ (Krier and Gunnarsson, 1995), which corresponds to $R_c = 6.6 \text{ \AA}$, i.e., too large to obtain an attractive interaction in the work of Lammert *et al.* (1995). If this is combined with the estimate of $U_0 \sim 2.7 \text{ eV}$ (see Sec. IV.A), a large and positive $U_{\text{met.scr.}} \sim 0.5 \text{ eV}$ [$\mu = N(0)U \sim 4$] results. This may suggest that it is important to allow for charge transfer to the molecule where the studied electrons are located, as is normally assumed for metallic systems.

An alternative electronic mechanism was suggested by Friedberg *et al.* (1992). They argued that it is favorable to form a two-electron wave function involving one t_{1u} and one t_{1g} state. In this way a correlated state can be formed, which lowers the Coulomb energy. Friedberg *et al.* (1992) argued that this more than outweighs the cost in one-electron energy. This two-electron state is bosonlike and forms a Bose band, which may lead to a Bose-Einstein condensate.

VI. BEYOND THE MIGDAL-ELIASHBERG THEORY

A. Migdal's theorem

Migdal's theorem states that vertex corrections in the electron-phonon interaction can be neglected if the typical phonon frequencies ω_{ph} are sufficiently smaller than the electronic energy scale, say the Fermi energy E_F (Migdal, 1958). This theorem is assumed to be valid in the derivation of the Eliashberg (1960) theory. For the fullerenes, the highest phonon frequency is about 0.2 eV , and the width of the t_{1u} band is about $1/2 \text{ eV}$, giving $E_F \sim 0.25 \text{ eV}$. Migdal's theorem may therefore be strongly violated for the fullerenes. If higher subbands are included, one may argue that E_F is much larger, but the conclusion that Migdal's theorem is violated remains correct (Gunnarsson *et al.*, 1994b).

The lowest-order vertex corrections were studied by Grabowski and Sham (1984), who calculated these corrections approximately and found that they could strongly reduce T_c . More recently, the issue has been studied extensively by Pietronero and co-workers (Pietronero and Strässler, 1992; Grimaldi *et al.*, 1995a, 1995b; Pietronero *et al.*, 1995). They introduced a theory that is nonperturbative in λ and perturbative in $m\lambda$, where $m = \omega_{\text{ph}}/E_F$. First the lowest-order vertex correc-

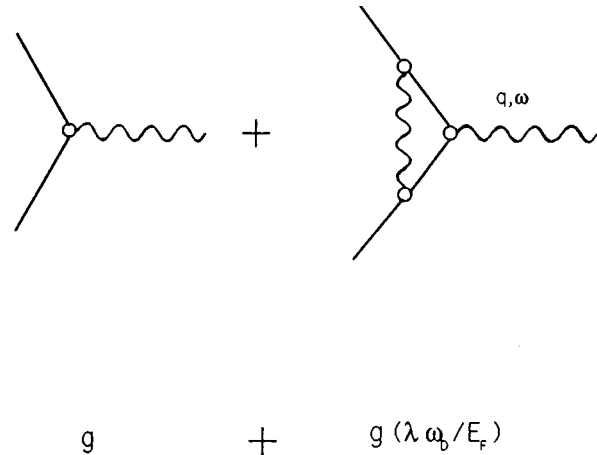


FIG. 12. The zeroth-order vertex and the first-order vertex correction. After Pietronero *et al.* (1995).

tion was calculated (see Fig. 12) for an electron-gas-like model. The result is shown in Fig. 13 for $m=1$ and as a function of ω and $Q = q/(2k_F)$, where ω and q are the Matsubara frequency and wave vector of the phonon line and k_F is the Fermi wave vector. The energy of the incoming electron was set to zero, and $\omega_0 = \omega_{\text{ph}}$ is the energy of the Einstein phonon. This should be compared with the zeroth-order contribution, which is unity. The vertex correction has a very strong Q dependence. For small $Q \neq 0$ and small ω it is large and negative, while it is positive elsewhere. This suggests that the influence on T_c may depend strongly on the system. An Eliashberg-like theory was then developed, including the lowest-order vertex correction and two “crossed” phonon lines in the scattering between two electrons (Grimaldi *et al.* 1995a, 1995b). Figure 14 shows their results for T_c and for the isotope effect

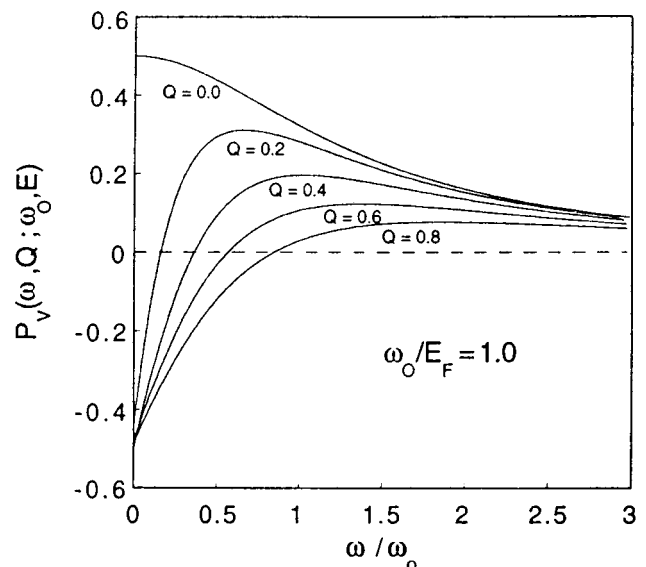


FIG. 13. Behavior of the vertex correction for different values of $Q = q/(2k_F)$. After Pietronero *et al.* (1995).

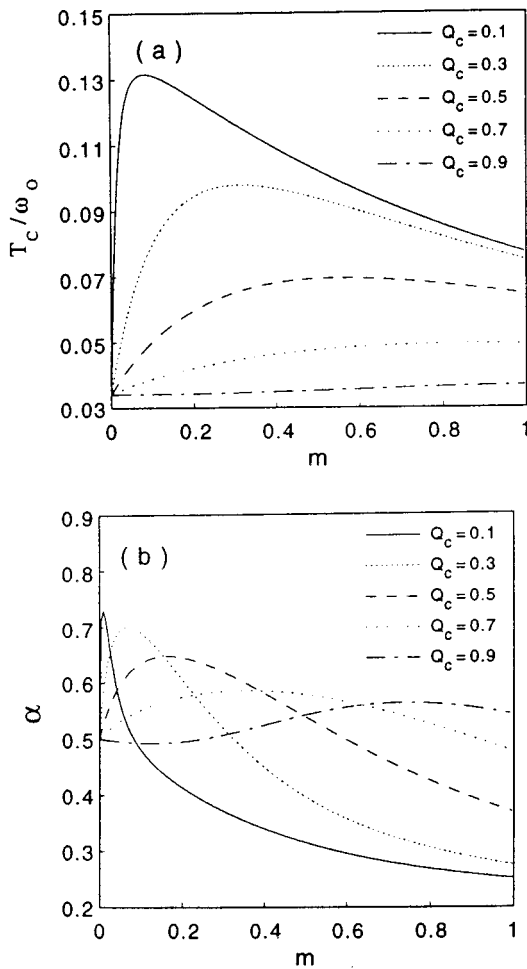


FIG. 14. (a) T_c as a function of $m \equiv \omega_{ph}/E_F$ and the cutoff momentum Q_c for $\lambda=0.5$. (b) Isotope-effect exponent α as a function of m and Q_c . After Grimaldi *et al.* (1995a, 1995b).

$$\alpha = -\frac{d \ln T_c}{d \ln M}, \quad (29)$$

where M is the carbon mass. These results were calculated assuming that there is a cutoff in q -space at some critical Q_c . It was argued (Grimaldi *et al.*, 1995a, 1995b) that this cutoff may simulate specific one-particle effects or correlation effects (Kulic and Zehyer, 1994). Depending on the value of Q_c , the theory may predict a large enhancement of T_c or no enhancement at all. It has been argued that a substantial enhancement of T_c due to the violation of Migdal's theorem may be an important reason why T_c is so much higher in A_3C_{60} than in intercalated graphite (Pietronero and Strässler, 1992). The value of the isotope effect can also vary substantially and may even be larger than 0.5. In the limit where Migdal's theorem is valid, this theory gives $\alpha=0.5$, since no Coulomb effects are included ($\mu^*=0$).

As described in Sec. V.B, Takada (1993) also considered corrections to Migdal's theorem and found that these enhance T_c for moderate values of the phonon frequencies. Ikeda *et al.* (1992) showed that Migdal's theorem becomes valid again when the phonon energies are much larger than the electronic energies. Kostur and

Mitrovic (1993) studied the vertex corrections with emphasis on two-dimensional systems, and Krishnamurthy *et al.* (1994) and Cappelluti and Pietronero (1996) studied systems with a van Hove singularity. Kostur and Mitrovic (1994) studied the corrections to T_c from vertex corrections for several model interactions. For a BCS type of interaction and an isotropic electron-phonon interaction, they found that vertex corrections reduce T_c , while for a highly anisotropic interaction, inspired by the cuprate superconductors, they found that T_c can also be enhanced by the vertex corrections. Asai and Kawaguchi (1992) argued that nonadiabatic effects could enhance the coupling by 10–30 %.

The violation of Migdal's theorem is also expected to play an important role in the photoemission spectrum. According to Migdal's theorem, the spectrum should just show single-phonon satellites. Due to various broadening effects, this cannot be checked experimentally for A_3C_{60} . Theoretical calculations suggest, however, that multiple satellites develop (Gunnarsson *et al.*, 1994a, 1994b). This involves a substantial transfer of spectral weight to higher binding energies, and the coupling to phonons and plasmons may explain (Knapfer *et al.*, 1993) the large observed width of the t_{1u} band in photoemission (C. T. Chen *et al.*, 1991).

The work above illustrates that the violation of Migdal's theorem could have important effects for the fullerides, but the magnitude, and perhaps even the sign, of the corrections are not fully established.

B. Jahn-Teller effects beyond Migdal-Eliashberg treatment

The threefold degeneracy of the t_{1u} level is lifted when a vibration of H_g symmetry is excited. This makes C_{60} molecules with a partly filled t_{1u} level unstable to a Jahn-Teller distortion (Jahn and Teller, 1937). It has been shown Auerbach *et al.*, 1994; Ihm, 1994; Manini *et al.*, 1994) that this Jahn-Teller system has a Berry phase (Berry, 1984), which imposes selection rules on the allowed transitions. These Jahn-Teller modes are included in the Migdal-Eliashberg theory under the assumption that the bandwidth is much larger than the phonon frequency. Below we discuss how, in the opposite limit, the molecular limit, some new interesting effects appear. These effects may possibly also be relevant for doped C_{60} compounds, although the bandwidth may be too large for these systems to allow the survival of the molecular properties.

It is interesting to study the energy of C_{60}^{n-} as a function of the electron-phonon coupling strength. A Jahn-Teller energy is defined as

$$E_{JT} = \sum_{\nu=1}^8 \frac{g_{\nu}^2}{\omega_{\nu}}, \quad (30)$$

where the sum is over the eight H_g modes, and g_{ν} and ω_{ν} are the coupling strength and energy, respectively, of the ν th mode. In the strong-coupling limit, the energy can then be written as (Lannoo *et al.*, 1991)

$$E^{SC}(n) = C(n)E_{JT}, \quad (31)$$

where $C(n) = 1$ ($n=1,5$), 4 ($n=2,4$), or 3 ($n=3$). It was emphasized by Yabana and Bertsch (1992), Auerbach *et al.* (1994), and Manini *et al.* (1994) that in the weak-coupling limit the prefactor in the energy expression is a factor $5/2$ larger,

$$E^{\text{WC}}(n) = \frac{5}{2} C(n) E_{\text{JT}}, \quad (32)$$

due to the Jahn-Teller effect, while for a mode of A_g symmetry the prefactors are identical. This result is valid for a free molecule or a solid with zero bandwidth, while the Migdal-Eliashberg theory is valid in the opposite limit of a large bandwidth. Auerbach *et al.* (1994) and Manini *et al.* (1994) observed that in the zero-bandwidth, weak-coupling limit, the attractive interaction between two electrons due to the electron-phonon interaction for C_{60}^{3-} ,

$$U_{\text{ph}}^{\text{WC}}(3) = -5 E_{\text{JT}}, \quad (33)$$

is a factor of 3 larger than in the Eliashberg theory. This could have important implications for the superconductivity. We notice, however, that for realistic estimates of the coupling constants, the system is not in the weak-coupling limit and may actually be closer to the strong-coupling limit (Gunnarsson, 1995). The prefactor in Eqs. (32) and (33) is then strongly reduced already in the zero-bandwidth limit.

VII. CALCULATED PROPERTIES

A. Transition temperature

It was pointed out very early that the estimated values of the electron-phonon coupling λ to the intramolecular modes are of the right order of magnitude to explain the transition temperature T_c (Varma *et al.*, 1991; Mazin *et al.*, 1992; Schluter *et al.*, 1992a, 1992b). Since the calculated values of λ are only intermediate, the quite high intramolecular phonon frequencies are important for the explanation of the rather high values of T_c . For values of λ in the upper range of the estimates, the rather large values of T_c can be understood even if it is assumed that the inefficient renormalization of μ^* by retardation effects in the fullerides leads to substantially larger μ^* than for conventional superconductors. For instance, Gunnarsson *et al.* (1995) solved the Eliashberg equation by using the coupling constants deduced from photoemission for free C_{60}^- molecules (see Sec. III.A.4), a t_{1u} bandwidth of $1/2$ eV, and the density of states at the Fermi energy deduced from NMR (see Sec. III.A.4). It was found that to reproduce the values of T_c for K_3C_{60} and Rb_3C_{60} , μ^* had to be 0.6, i.e., even larger than the estimate in Sec. V.B. We note that the value 0.6 used in the Eliashberg equation corresponds to the value 0.4 in the McMillan formula, due to renormalization effects inside the t_{1u} band. From the discussion in the previous sections it is clear, however, that the uncertainties in the estimates of λ and μ^* are substantial and the use of the Migdal-Eliashberg theory introduces further uncertainties.

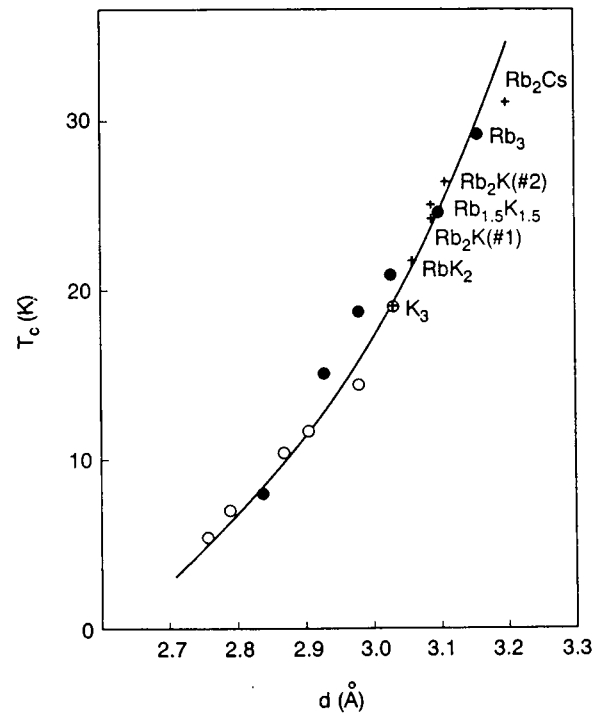


FIG. 15. Variation of T_c with the shortest distance d between the two closest carbon atoms on neighboring C_{60} molecules. ●, ○, +, experimental; solid line, theoretical. The density of states was assumed to have a power-law dependence on d , $N(0) \sim d^n$, with $n=2.7$ adjusted to fit experimental results. After Schluter *et al.* (1992b).

Zheng and Bennemann (1992) studied the effect of having phonon energies comparable to the bandwidth. They used the Eliashberg theory, i.e., Migdal's theorem was implicitly assumed to be valid, but they did not assume the bandwidth to be large in the solution of the Eliashberg theory. They found that the quasiparticle weight was less renormalized than is normally assumed [the weight was larger than $1/(1+\lambda)$]. As a result their calculated value of T_c was larger than that obtained with the McMillan (1968) formula.

1. Lattice-parameter dependence

As discussed in Sec. II.A for the A_3C_{60} superconductors, except for Cs_3C_{60} , T_c increases with the lattice parameter. The explanation of this behavior was provided very early (Fleming *et al.*, 1991; Varma *et al.*, 1991; Mazin *et al.*, 1992; Schluter *et al.*, 1992a; 1992b; Zhou *et al.*, 1992). As discussed in Sec. III.A.2, for the coupling to the intramolecular phonons, to a very good approximation $\lambda = VN(0)$ can be factorized into an intramolecular part V and the density of states $N(0)$ (Lannoo *et al.*, 1991). The intramolecular part V can be expected to be essentially independent of the lattice parameter a , while $N(0)$ grows with a . This follows, since, as a increases, the overlap between the molecules is reduced, leading to a reduced bandwidth and an increased density of states. Figure 15 shows a calculation of T_c based on a tight-binding calculation of $N(0)$, which as-

sumes a power-law reduction of the hopping-matrix elements with the separation between the closest atoms on neighboring molecules (Schluter *et al.*, 1992b). The exponent of the power law was adjusted to fit experimental results. The resulting density of states ratio $N(0)$ (Rb_3C_{60})/ $N(0)$ (K_3C_{60})=1.12 is smaller than the calculated values in Table V but close to the ratio 1.13 derived from NMR (Antropov, Mazin, *et al.*, 1993).

The very strong variation of T_c with the lattice parameter a in $\text{Na}_2\text{AC}_{60}$ (see Fig. 3) suggests a strong variation of $N(0)$ with a in this system (see, Yildirim, Fischer, *et al.*, 1995). Indeed, Maniwa *et al.* (1995) deduced $N(0)$ from the NMR relaxation rate for $\text{Na}_2\text{AC}_{60}$ ($A=\text{K}, \text{Rb}, \text{Cs}$) at ambient pressure and found a much stronger dependence than for the $Fm\bar{3}m$ structure, although possibly not quite strong enough to fully explain the strong variation of T_c . However, simple tight-binding calculations that included 60 “radial” p -orbitals per C_{60} molecule did not give a very different a dependence for the density of states for the two structures (Gunnarsson, 1993). It has instead been suggested that $\text{Na}_2\text{KC}_{60}$ and $\text{Na}_2\text{RbC}_{60}$ may have structural distortions and that these distortions could reduce $N(0)$ much more than changes in the lattice parameter (Maniwa *et al.*, 1995). Since the Fermi energy falls fairly close to a maximum in the density of states in the undistorted $Pa\bar{3}$ structure (Satpathy *et al.*, 1992), such a reduction is possible. An intermediate a dependence was observed in pressure experiments for $\text{Na}_2\text{CsC}_{60}$ (Mizuki *et al.*, 1994), which is possibly consistent with the observation that the structure may also distort under pressure (Zhu, 1995; Fischer, 1996). Whether $N(0)$ in the ideal structure has a strong dependence on a or the strong dependence could be explained by other factors remains an interesting issue. For instance, it has also been proposed that paramagnetic impurities may suppress T_c in $\text{Na}_2\text{KC}_{60}$ and $\text{Na}_2\text{RbC}_{60}$ (Tanigaki and Prassides, 1995).

2. Doping dependence

As discussed in Sec. II.A, Yildirim *et al.* (Yildirim, Barbedette, *et al.*, 1995; Yildirim, Barbedette, Fischer, Lin, *et al.*, 1996; Yildirim, Barbedette, Fischer, Bendele, *et al.*, 1996) have found a strong doping (n) dependence for T_c by studying $\text{Na}_2\text{Cs}_x\text{C}_{60}$ ($n \leq 3$) and $\text{Rb}_{3-x}\text{Ba}_x\text{C}_{60}$ ($n \geq 3$). They found a maximum for T_c close to half-filling ($n=3$) and rapid decrease as n was reduced or increased. The reduction for $n > 3$ may be explained by considering the density of states for a system with mero-hedral disorder (Yildirim, Barbedette, *et al.*, 1995). The density of states shows a steady reduction with energy, except at the bottom of the band (Gelfand and Lu, 1992a, 1992b). As the filling n is increased, the density of states at the Fermi energy $N(0)$ then drops, and λ is reduced, which may explain the drop in T_c . It appears, however, that there is no such explanation for $n < 3$. A tight-binding calculation for the appropriate structure ($Pa\bar{3}$) shows an increase in the density of states as the energy is lowered (Satpathy *et al.*, 1992). The situation is changed slightly if the potential from the alkali atoms is

taken into account (Gunnarsson, 1996). The nearest alkali neighbors of a given C_{60} molecule create a potential with $l=4$, which cannot be efficiently screened by the C_{60} molecule and which modifies the density of states. Since the density of states is sampled over a finite energy, due to the rather large phonon energies, the density of states nevertheless effectively grows as the energy is reduced. One might have expected the potential of the vacancies to strongly influence the density of states; however, it has mainly monopole or dipole character relative to neighboring C_{60} molecules, and it is therefore efficiently screened. Thus the drop in T_c as n is reduced appears not to be understood.

B. Isotope effect

As discussed in Sec. II.C, different experiments give widely different results for the isotope effect ($T_c \sim M^{-\alpha}$), with α even taking on values larger than unity. In the case of almost complete substitution, $\alpha=0.30$ was found for K_3C_{60} and Rb_3C_{60} (Chen and Lieber, 1992).

Early on it was pointed out that a reasonable value of $\alpha \sim 0.3$ can be obtained if the mechanism for superconductivity is assumed to be the interaction with the intramolecular phonons (Schluter *et al.*, 1992b). For instance, from the McMillan formula [Eq. (1)], the prefactor ω_{ph} gives $\alpha=0.5$, and the renormalization of μ^* as defined in Eq. (17) gives a reduction of α . Thus α is reduced to about 0.3 if it is assumed that $\mu^* \sim 0.2$ and $\omega_{\text{ph}} \sim 1000 \text{ cm}^{-1}$. We note, however, that the McMillan formula is not very accurate for calculating the isotope effect. The isotope effect was also calculated in the model discussed in the previous section (VII.A) using the Eliashberg theory and the coupling constants derived from photoemission (Gunnarsson *et al.*, 1995). The values of α were then found to be 0.32 and 0.37 for K_3C_{60} and Rb_3C_{60} , respectively.

Deaven and Rokhsar (1993) addressed the large spread in the experimentally observed isotope effect α for different isotope substitutions. They considered a model with harmonic phonons and a linear electron-phonon coupling. Within the Migdal-Eliashberg framework, they showed that the anomalous isotope effect cannot be explained. In particular, they showed that λ is independent of the isotope distribution. Anharmonic effects have been considered, e.g., by Crespi *et al.* (1991) and Inada and Nasu (1992). These effects could in principle lead to $\alpha > 0.5$.

The isotope effect has traditionally been considered a sign of an electron-phonon mechanism. It has, however, been pointed out that, even for an electronic mechanism, there is an isotope effect due to the change of the electronic structure by zero-point vibrations (Chakravarty, Kivelson, *et al.*, 1992; Ashcroft and Cyrot, 1993). Ashcroft and Cyrot (1993) emphasized the opposing effects of the translational phonons and the librations on the electronic structure. They argued that an increase in the carbon mass would tend to reduce the hopping integral due to the translational vibrations but would also increase it due to the librations. They found that, depending on the precise assumptions about the parameters, α could take on a broad range of values, including

values larger than 0.5. In view of this it is not clear how much is proven by the reasonable values for α found from the intramolecular phonons alone.

C. Reduced gap

The superconductivity gap Δ is of interest, since it may give indications about strong-coupling effects. Gunnarsson *et al.* (1995) calculated the gap using the Eliashberg equation in the model discussed above and using the couplings deduced from photoemission. They obtained the values $2\Delta/T_c = 3.59$ and 3.66 for K_3C_{60} and Rb_3C_{60} , respectively. This is fairly close to the BCS value 3.52 , while the experimental values range from about the BCS value up to about 4.2 .

The much larger values found in point-contact tunneling measurements have stimulated a substantial amount of work. Mazin, Dolgov, *et al.* (1993) studied a model with coupling to both intramolecular phonons (with frequencies around 1000 cm^{-1}) and low-lying modes with frequencies of the order 40 cm^{-1} . The latter modes could be librations or intermolecular or alkali modes. Due to the huge difference between the frequencies, this model shows very interesting properties. The low-lying modes hardly influence T_c , but they have a strong influence on the reduced gap $2\Delta/T_c$. Thus Mazin, Dolgov, *et al.* (1993) could use typical couplings to the intramolecular modes ($\lambda_1 \sim 0.5$) to produce the measured values of T_c but at the same time use strong coupling to the low-lying modes ($\lambda_2 \sim 2.7$) to produce a large reduced gap ($2\Delta/T_c \sim 5$). More recent work has suggested that the coupling to the low-lying modes is much weaker (see Secs. III.B, C, and D) and that the reduced gap may be much smaller than that found in point-contact tunneling. The model of Mazin, Dolgov, *et al.* (1993) may therefore not be applicable to A_3C_{60} , but it is still a nice illustration of the unconventional properties that can be obtained if bosons of very different energies couple to the electrons.

Mele and Erwin (1993) considered the detailed Fermi surface for a system with *ordered* molecules. They studied an axial, nodeless order parameter with d symmetry. This led to the ratio $2\Delta/T_c \sim 4.6$. The temperature dependence and the quasiparticle spectrum were also non-BCS. Since the solution, however, depends on specific features of the Fermi surface, it is not clear if it survives for the disordered system.

Mele *et al.* (1994) studied the effects of orientational disorder and found that it introduces some gap anisotropy. Furthermore, they obtained some reduction of both T_c and Δ in such a way that the reduced gap $2\Delta/T_c$ was increased to values of the order of 3.8 – 4.0 . They therefore concluded that disorder can lead to an increased gap ratio even within a weak-coupling theory.

D. Other properties

Erwin and Pickett (1991) calculated the Fermi velocity v_F for a system of ordered C_{60} molecules, using the local-density approximation. From $v_F = 1.8 \times 10^7\text{ cm s}^{-1}$

they deduced the Drude plasma energy $\hbar\Omega = 1.2\text{ eV}$ and the clean-limit London penetration depth $\lambda = 1600\text{ \AA}$. Considering that A_3C_{60} is in the dirty limit, they corrected this result by a factor $(1 + \xi/l)^{1/2}$, where ξ is the coherence length and l is the mean free path. Using $\xi = 26\text{ \AA}$ and $l = 10\text{ \AA}$, they obtained $\lambda \sim 3000\text{ \AA}$, in reasonable agreement with experiment (the scattering between different experiments is, however, large).

VIII. CONCLUDING REMARKS

It is widely believed that A_3C_{60} ($A = K, Rb$) are s -wave BCS-like superconductors, driven by the coupling to the intramolecular H_g phonons and probably with some strong-coupling effects. The work reviewed here is consistent with and supports such a picture, although there is no conclusive evidence that this picture is correct or that an electronic mechanism is excluded. Accurate and detailed tunneling data would be very useful in this context.

It appears to be understood why A_3C_{60} are metals and not Mott-Hubbard insulators, in spite of the large Coulomb interaction. Experimental and theoretical estimates of the electron-phonon coupling λ give values of about 0.5 – 1 . For the other important parameter determining T_c , the Coulomb pseudopotential μ^* , there are arguments that μ^* is not strongly renormalized by retardation effects due to scattering of the electrons into subbands other than the t_{1u} band. This, however, leaves unresolved questions about the screening and retardation effects on μ^* within the t_{1u} band. Theoretical calculations of T_c based on estimates of λ and μ^* are consistent with experiment and support an electron-phonon picture.

The lattice-parameter dependence of T_c seems to be understood for A_3C_{60} in the $Fm\bar{3}m$ structure but not for Na_2AC_{60} in the $Pa\bar{3}$ structure. The doping dependence is also not well understood. The BCS-like superconducting gap seen in most experiments follows from the picture of the superconductivity's being driven by the H_g intramolecular phonons, while the isotope effect still gives rise to some interesting experimental and theoretical questions.

We have emphasized that because several energy scales are comparable, the theoretical treatment of the fullerides is particularly demanding but also unusually interesting. Thus one may expect Migdal's theorem to be violated and many-body effects due to the Coulomb interaction to be important. The electron-phonon interaction should also be important for many properties. On the other hand, the molecular-solid character leads to certain simplifications, for instance the electronic properties are expected to be dominated by the threefold-degenerate t_{1u} orbital. Due to the unusual parameter range, many interesting general issues are raised in a particularly clearcut way for the doped fullerides, and their solutions should have implications in many other fields.

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