Nonadiabatic high-T_c superconductivity in hole-doped fullerenes

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In this paper we address the possibility of high-T_c superconductivity ($T_c \sim 100$ K) in hypothetical hole doped C_{60} within the context of the nonadiabatic theory of superconductivity. Our analysis shows that electron doped fullerenes, represented by the A_3C_{60} family, are characterized by relatively small values of the electron–phonon coupling constant λ, which can thus be further increased by hole doping before lattice instabilities occur. In particular we show that T_c larger than 100 K are compatible in the nonadiabatic context with microscopic parameters $\lambda_h \simeq 0.5-1.0$, $\mu^* \simeq 0.3-0.5$ and phonon frequencies $\omega_{ph} \simeq 1500-2000$ K. These results provide a stimulus for material engineering and optimization along the lines indicated.

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Improving the superconducting properties of real systems, in particular the critical temperature T_c, is one of the primary focal objectives in the field of material science. This path has been extensively scoured for the so-called conventional low temperature superconductors (LTSC), where the main tuning parameter for T_c was the electron–phonon (el–ph) coupling constant λ. In spite of the fact that many LTSC compounds were characterized by a sizable λ (see Fig. 1), the maximum critical temperature found along this way was $T_c \simeq 23$ K in Nb_3Sn, and there was a common filling that higher T_c were bounded by an upper limit 20–25 K before lattice instabilities occur.[9]

The discoveries of superconductivity in cuprates ($T_c^{max} \simeq 135$ K), in fullerenes ($T_c^{max} \simeq 40$ K), and recently in MgB_2 ($T_c \simeq 40$ K) clearly indicate that such an empirical limit does not apply in these unconventional superconductors, so that T_c could be in principle further increased. The answer to this possibility however strongly depends on the assessment about the microscopic origin of superconductivity in these compounds.

A controlled way to tune T_c in the A_3C_{60} family is through the hydrostatic pressure or through the "chemical pressure" ruled by the size of the alkali ion A[8]. In both these experiments the value of T_c is mainly affected by the corresponding density of states $N(E_F)$: applying of pressure ("chemical" or hydrostatic) reduces the lattice spacing a, increasing the electronic bandwidth and reducing $N(E_F)$. This way to enhance T_c by increasing a seems however limited since for sufficiently high $a \gtrsim 14.5$ Å the materials loose their metallic properties and hence superconductivity. An alternative way to enhance the density of states, and λ and T_c by consequence, would be on the other hand a hypothetical doping with hole charges.[6,7] This perspective is however realistic only if the loss of metallic behavior at large a is not related to a particularly high λ but to other physical reasons, as strong correlation effects.[10]

In this paper we discuss the possibility to achieve high-T_c superconductivity in new fullerene compounds based on positive charge doping. We show that in the framework of the nonadiabatic theory of superconductivity there is no intrinsic limitation to a further enhancement of T_c up to $T_c \sim 100$ K with realistic values of the coupling constant λ, $\lambda_e \simeq 0.4-0.8$ for electron doped systems and $\lambda_h \simeq 0.6-1.2$ for hole doped ones.

Nonadiabatic effects arise when the energy scale of electron dynamics, parametrized by the Fermi energy E_F, is small and comparable with the phonon frequency scale

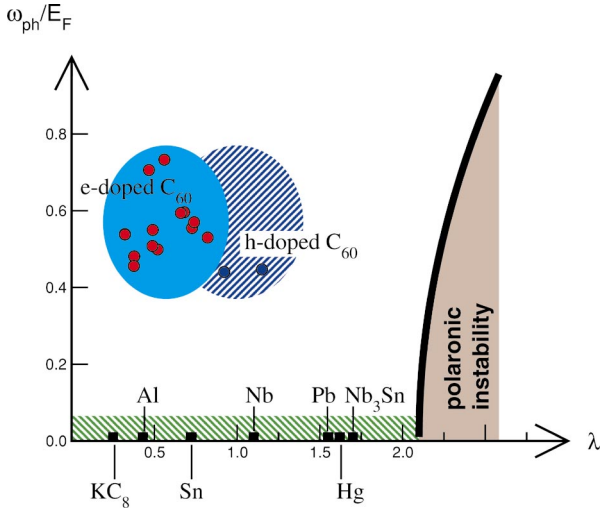

FIG. 1. (Color) Schematic phase diagram of the C_{60} compounds in terms of the el–ph coupling λ and the adiabatic ratio ω_{ph}/E_F. Filled blue region represents electron doped compounds, the dashed area the hole doped ones. Red and blue dots mark numerical calculations available in literature, respectively, for electron and hole doped fullerenes (Refs. 1–7). Standard values were used for the density of states $N(E_F)=10$ states/(eV-spin-C_{60}) (electron doping) and $N(E_F)=16.7$ states/(eV-spin-C_{60}) (hole doping), and $E_F=0.25$ for both the Fermi energies (Ref. 8). Migdal–Eliashberg (ME) theory holds true only around the $\omega_{ph}/E_F=0$ axis (green area). For strong el–ph coupling λ the systems are expected to undergo polaronic instabilities.

$\omega_{\rm ph}$.[11–13] This is indeed the case of C_{60} compounds which are characterized by a set of very narrow bands with typical $E_F \simeq 0.25$ eV, for both electron and hole doping, whereas phonon mode energies range up to $\simeq 0.2$ eV.[8]

In the microscopic parameter space this new nonadiabatic regime can be defined in terms of the electron–phonon (el–ph) coupling λ and of the adiabatic ratio $\omega_{\rm ph}/E_F$. In Fig. 1 we show the estimated physical regions for both electron and hole doped C_{60} compounds (respectively, filled and dashed blue regions). Red dots represent several numerical calculations of negative charged C_{60}.[1–5] Note that a large adiabatic ratio $\omega_{\rm ph}/E_F$ is estimated for both the electron and hole doped compounds due to the narrowness of the electronic bands, violating the assumptions of the Migdal–Eliashberg (ME) theory which is valid only around the $\omega_{\rm ph}/E_F=0$ axis (green region in the figure).[9] Note moreover that the value of λ in fullerenes is not much larger than other strong-coupling ME materials as Pb, Hg or Nb_3Sn, which however show relatively small T_c's ($T_c \lesssim 23$ K).

In this situation we claim that the finite adiabatic ratio and the consequent onset of *nonadiabatic channels* are the fundamental ingredients of high critical temperature more than extremely large values of λ. A nonadiabatic approach appears thus the unavoidable starting point for any realistic and intrinsically consistent description of the superconductivity in C_{60} based materials.

Theoretical tools of our investigation will be the generalized equations of superconductivity in nonadiabatic regime:[11–14]

$$Z(\omega_n) = 1 + \frac{T_c}{\omega_n} \sum_{\omega_m} \Gamma_Z(\omega_n, \omega_m)\, \eta_m, \tag{1}$$

$$Z(\omega_n)\Delta(\omega_n) = T_c \sum_{\omega_m} \Gamma_\Delta(\omega_n, \omega_m) \frac{\Delta(\omega_m)}{\omega_m}\, \eta_m, \tag{2}$$

where the kernels $\Gamma_Z(\omega_n,\omega_m)$ and $\Gamma_\Delta(\omega_n,\omega_m)$ contain the nonadiabatic el–ph channels[11–13] (vertex and cross Feynman's diagrams) arising from the breakdown of Migdal's theorem:[15]

$$\Gamma_Z(\omega_n,\omega_m) = \lambda(\omega_n-\omega_m)[1+\lambda P(\omega_n,\omega_m,Q_c)],$$

$$\Gamma_\Delta(\omega_n,\omega_m) = \lambda(\omega_n,\omega_m)[1+2\lambda P(\omega_n,\omega_m,Q_c)] + \lambda^2 C(\omega_n,\omega_m,Q_c) - \mu,$$

where $\lambda(\omega_n-\omega_m) = 2\int d\omega\, \alpha^2F(\omega)\omega/[\omega^2+(\omega_n-\omega_m)^2]$ and $\alpha^2F(\omega)$ is the el–ph spectral function.

Eqs. (1) and (2) can be parametrized in terms of few physical quantities, as the el–ph coupling $\lambda=\lambda(\omega_n=0,\omega_m=0)$, the characteristic phonon energies $\omega_{\rm ph}$ and the Coulomb repulsion μ. The dependence over the Fermi energy, which we set equal to $E_F=0.25$ eV in agreement with experimental and theoretical evaluations, is via the finite bandwidth factor $\eta_m = 2\arctan\{E_F/[Z(\omega_m)\omega_m]\}$ and the nonadiabatic terms P and C which play the primary role in nonadiabatic superconductivity. To illustrate this point let us consider a small $\omega_{\rm ph}/E_F$ expansion of the vertex function P for an Einstein phonon spectrum with frequency $\omega_{\rm ph}$:

$$P \simeq \frac{\omega_{\rm ph}}{E_F Q_c^2}\left[\left|\arctan\frac{\omega_n}{\omega_{\rm ph}} - \arctan\frac{\omega_m}{\omega_{\rm ph}}\right| - Q_c^2\right]. \tag{3}$$

The above approximate expression applies when $4\omega_{\rm ph}/E_F Q_c^2 < 1$, where $0 < Q_c \leqslant 1$ is a dimensionless momentum cutoff in the exchanged phonon scattering which takes into account the effect of strong electronic correlations:[16–18] $Q_c \simeq 1$ when correlation is weak while $Q_c \to 0$ when the system approaches a metal-insulator transition from the metallic side.[16,17] As it is clear from Eq. (3), when Q_c is small, the vertex function P acquires an overall positive sign which leads to an enhancement of the effective el–ph coupling parametrized by Γ_Δ and Γ_Z. A similar behavior is followed also by the nonadiabatic cross term C. Numerical calculations[10] of the critical correlation strength give $U_c \sim 1.5$–1.7 eV while photoemission measurements[8] of the Hubbard repulsion find $U \sim 1.4$–1.6 eV. Fullerenes are therefore believed to be very close to the metal-insulator transition, so that Q_c should be relatively small implying therefore that P and C have positive sign. For the moment we shall consider $Q_c=0.2$ as a representative case of strong correlation. A detailed study of the dependence of our results on Q_c is later discussed.

Eqs. (1) and (2) have been used as starting point to analyze the superconducting properties of electron-doped fullerenes as Rb_3C_{60}.[14] In particular the nonadiabatic theory was shown in Ref. 14 to provide a much more realistic analysis for this compound than the conventional ME theory. For instance, the high-T_c value $T_c=30$ K and the isotope coefficient $\alpha_{T_c}=0.21$ in Rb_3C_{60} were shown to be consistent with a moderate value $\lambda_e \lesssim 1$ of the el–ph coupling constant for this electron-doped compound, in agreement with numerical and LDA calculations,[1–5] whereas the conventional ME theory would predict $\lambda_e \gtrsim 1$.[14] An important role in this nonadiabatic framework is played by the tendency in strongly correlated systems as fullerenes towards a predominance of small momentum scattering,[16–19] parametrized by Q_c. This feature, which selects positive regions of the vertex function and gives rise to an effective enhancement of the el–ph pairing, is a peculiar effect which is usually neglected in the local approximation enforced by dynamical mean-field theory techniques.[20] A consistent nonadiabatic analysis cannot disregard these effects. Our approach, which goes beyond such a local approximation by introducing an average effect of Q_c, should thus be considered complementary with respect to DMFT which is often used to investigate different microscopic mechanisms responsible for high-T_c superconductivity based on spin exchange, Jahn–Teller coupling or on the vicinity to a Mott–Hubbard transition.[21,22]

The above results obtained for Rb_3C_{60} in a nonadiabatic context provide a much more promising basis to find high-T_c superconductivity in fullerenes by increasing λ than ME theory. It is indeed clear that if $T_c \sim 30$–40 K in the A_3C_{60} family would stem from a particularly large $\lambda_e \gtrsim 1$, as in the ME analysis, there would be few chances to improve significantly the critical temperature and to prevent the occurrence of lattice instabilities. In order to quantify these concepts we show in Fig. 2 the behavior of the critical temperature as

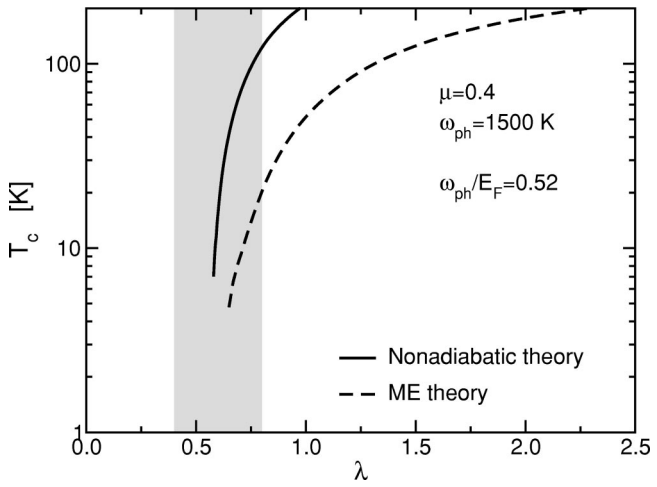

FIG. 2. T_c versus el−ph coupling λ for both ME theory (dashed line) and nonadiabatic theory (solid line). The shaded area represents the range of numerical calculations for λ in A_3C_{60} (see Fig. 1).

function of λ for both the nonadiabatic (solid line) and ME theory (dashed line) in the simple case of an Einstein phonon spectrum $\omega_{ph}=1500$ K and $\mu=0.4$. The shaded area in Fig. 2 corresponds to numerical and LDA estimates of λ_e for the A_3C_{60} compounds (see Fig. 1). As above discussed, in nonadiabatic theory relatively high values of T_c can naturally be accounted for with moderate values of the coupling λ in agreement with numerical estimates (gray region). More interesting, Fig. 2 suggests that critical temperatures as high as 100 K can be reached with a relative small increase of λ remaining yet in *a weak-intermediate regime*, far away from the region in which structural instabilities are expected to occur. On the opposite, critical temperatures of the order of $T_c\sim 100$ K can be recovered in the ME framework only by assuming an enhancement λ of a factor 2, in a range of a total coupling $\lambda\gtrsim 1.5$.

From theoretical point of view, one way to enhance the density of states, and correspondingly λ, in C_{60} compounds is given by considering positive charge transfer (holes) between dopant and C_{60} instead of negative ones (electrons). Leading modifications are expected to arise, for fixed lattice parameter, from the different degeneracy of the LUMO and HOMO bands of the C_{60} crystal, corresponding respectively to electron and hole doping. From a rough estimate, the ratio between the degeneracy of hole (five) and electron (three) bands would be thus reflected in a ratio $\lambda_h/\lambda_e\simeq 5/3$. Recent LDA calculations, which include possible changes in the el–ph matrix elements *g*, give a slightly smaller value $\lambda_h/\lambda_e\simeq 1.4$.[6,7]

In similar way we can expect significant enhancement of the T_c in a hypothetical positive charged C_{60} by increasing the lattice parameter. The effects of lattice expansion can be schematized, in the physical range of expansion, as a overall shrinking in energy of the whole set of bands.[23,24] The density of states and the Fermi energy would thus change as $[dN(E_F)/N(E_F)]=-[dE_F/E_F]=s[da/a]$, where the value of the slope *s* has been estimated by LDA calculations $s\sim 12$.[24]

In order to quantify the enhancement of T_c in a hypothetical hole doped C_{60}^{5+} (half-filled h_u valence bands) solid we consider a theoretical model able to properly describe the dependence of the superconducting properties on the hole doping and on the lattice expansion. To this aim we start from the microscopic values of λ and ω_{ph} needed to reproduce the experimental constraints of $T_c=30$ K and $\alpha_{T_c}=0.21$ for Rb_3C_{60} as calculated in Ref. 14. Then, assuming as fixed parameters of our model the LDA calculations for $s\sim 12$ and for $\lambda_h/\lambda_e\simeq 1.4$, we calculate the microscopic parameters λ, ω_{ph} and the corresponding critical temperatures T_c for hypothetical hole doped C_{60}^{5+} compounds. As simplified scheme we use a single mode phonon Einstein with frequency ω_0 scanning the range 400 K$\lesssim\omega_{ph}\lesssim$2000 K. This analysis provides thus the upper limit of the realistic phonon spectrum when $\omega_0\simeq 2000$ K and a consequent lower limit for the el–ph coupling λ_h. In addition we also compare our results with a continuum constant el–ph spectrum $\alpha^2F(\omega)=$const, 400 K$\lesssim\omega\lesssim$2000 K. The requirement that our analysis has to reproduce the experimental constraints for the electron doped Rb_3C_{60} leads to different values of the critical temperatures for each given pair of microscopic parameters (λ,ω_{ph}) establishing a one-to-one correspondence between T_c, λ, ω_{ph}.

In the inset of Fig. 3(a) are shown the microscopic starting parameters ω_{ph}−λ estimated by either the nonadiabatic (filled symbols) and ME theory (empty symbols) for two hypothetical hole doped C_{60} compounds with lattice constants, respectively, equal to K_3C_{60} (filled and empty triangles up, $a=14.253$ Å) and Rb_3C_{60} (filled and empty diamonds, $a=14.436$ Å). Here, ω_{ph} represents the logarithmic phonon average ω_{ln}. For the Einstein spectrum ω_{ph} coincides with the single mode energy.

In Figs. 3(a) and 3(b) we report the critical temperatures T_c as function of λ_h and ω_{ph}, respectively, predicted by both ME and the nonadiabatic theory for the above-mentioned positive charged C_{60}. Here, the empty squares represent the rectangular spectrum $\alpha^2F(\omega)$. The dependence of the critical temperature on the microscopic parameters in a hole-doped C_{60} compound leads to a complex behavior of T_c vs λ [see Fig. 3(a)] with the appearance of a maximum value of T_c in the framework of nonadiabatic theory for intermediate coupling $\lambda\sim 0.6-0.7$ whereas in ME theory T_c increases in a monotonic way by decreasing λ. The relation between λ and ω_{ph} shown in the inset of Fig. 3(a) produces a one-to-one correspondence between the data in Fig. 3(a) and Fig. 3(b). In particular in both theories the largest values of λ, compatible with the starting constraints, correspond to smallest phonon frequencies $\omega_{ph}\simeq 400$ K here considered whereas decreasing λ quickly enhances ω_{ph}.

Figure 3 shows that ME theory would predict high-T_c superconductivity ($T_c\sim 50-70$ K) in hole doped C_{60} compounds only under the extreme conditions $\lambda_h\sim 2-3$ and $\omega_{ph}\gtrsim 1500$ K. On the one hand, these extremely high values of λ are questioned by structural stability reasons. On the other hand, the high value of the relevant phonon frequencies $\omega_{ph}\gtrsim 1500$ required by this analysis would point toward

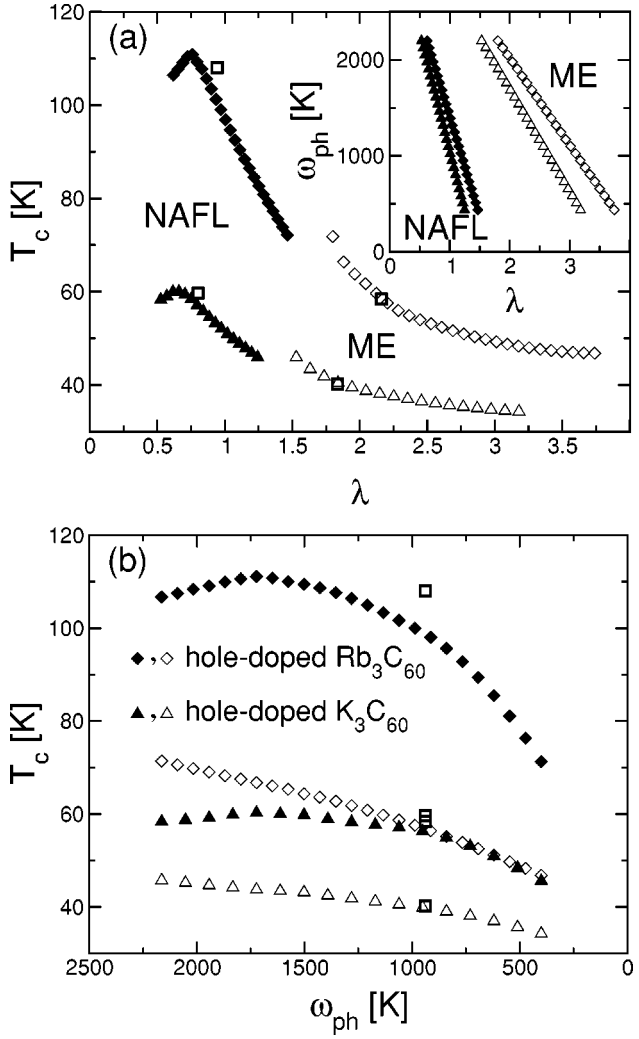

FIG. 3. Behavior of T_c as function either of λ_h [panel (a)] and of ω_{ph} [panel (b)] in the nonadiabatic theory (filled symbols) and in ME scenario (empty symbols). Diamonds correspond in both theories to a positive charged C_{60} with the same lattice parameter as Rb_3C_{60}, whereas the triangles describe a hypothetical hole doped C_{60} compound with the same lattice parameter as K_3C_{60}. Diamonds and triangles represent Einstein phonon spectra while the empty squares a rectangular spectrum (see text).

nonadiabatic effects ($\omega_{\mathrm{ph}}/E_F \simeq 0.52$) which are intrinsically inconsistent with ME theory and which could not be neglected.

A much more reasonable framework is recovered in the context of the nonadiabatic theory. Here the el–ph coupling for hypothetically hole doped C_{60} compounds would range from $\lambda_h \simeq 0.5-1.2$ for the lattice constant of K_3C_{60} and $\lambda_h \simeq 0.6-1.5$ for Rb_3C_{60} with critical temperature as high as $T_c \sim 100$ K (corresponding values of μ are $\mu \simeq 0.3-0.5$ in agreement with analytical and numerical estimates $\mu^* \simeq 0.4$[8]). It should be noted that the most promising enhancement of T_c for hole doped compounds would be achieved for the moderate values of $\lambda_h \sim 0.5-1.0$ coupled with high phonon frequencies $\omega_{\mathrm{ph}} \sim 1500-2200$ K, in agreement with the nonadiabatic scenario. Once more, it should be underlined that the high-T_c superconductivity is more related to a sizable nonadiabatic ratio within the nonadiabatic theory than to some extreme strong coupling conditions.

TABLE I. Dependence of λ, μ^* on the correlation parameter Q_c for an Einstein phonon $\omega_{\mathrm{ph}} = 1800$ K, in the case of an hypothetical hole doped C_{60} with the same lattice parameter of K_3C_{60} (left-hand side) and of Rb_3C_{60} (right-hand side).

	Hole-doped K_3C_{60}			Hole-doped Rb_3C_{60}		
Q_c	λ_h	μ^*	T_c (K)	λ_h	μ^*	T_c (K)
0.1	0.49	0.23	50	0.58	0.28	84
0.2	0.59	0.31	58	0.69	0.37	106
0.3	0.77	0.39	74	0.91	0.48	159
0.4	0.91	0.4	80	1.07	0.48	196

Finally, the sensitivity of the above analysis on the particular choice of the correlation parameter Q_c has also been investigated. Results are shown in Table I for an Einstein phonon $\omega_{\mathrm{ph}} = 1800$ K, in the case of a positive charged C_{60} with the same lattice parameter either of K_3C_{60} (left-hand side) and of Rb_3C_{60} (right-hand side). We see that the nonadiabatic theory predicts a $\lambda_h \lesssim 1$ and $\mu^* \lesssim 0.5$, also for the highest T_c compound as long as $Q_c \lesssim 0.4$ which corresponds to a correlation radius $\xi \gtrsim 25$ Å. Experimental measurements of ξ are thus welcome concerning this point.

In conclusion we have shown that significant enhancements of the critical temperature T_c in hole doped C_{60} compounds are a realistic possibility in fullerenes within the context of the nonadiabatic theory, while similar enhancements appear unrealistic if superconductivity in these materials would be actually described by the conventional ME theory. Values of the critical temperature of the order of 100 K can be consistently explained by the nonadiabatic nature of the el–ph superconductivity in these materials. The key parameter is the adiabatic ratio $\omega_{\mathrm{ph}}/E_F \simeq 0.5$ as discussed in Fig. 1. The scenario here discussed opens a new path to search for high-T_c superconductivity based on the nonadiabatic pairing in hole doped C_{60}. Recent works provide realistic perspectives for hole charged C_{60} compounds, either by chemical doping with acceptors[25] or by charge transfer to monolayers of C_{60} on substrates.[26]

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[1] C. M. Varma, J. Zaanen, and K. Raghavachari, Science **254**, 989 (1991).

[2] M. Schluter, M. Lannoo, M. Needels, G. A. Baraff, and Tománek, Phys. Rev. Lett. **68**, 526 (1992).

[3] M. Schluter, M. Lannoo, M. Needels, G. A. Baraff, and D. Tománek, J. Phys. Chem. Solids **53**, 1473 (1992).

[4] J. C. R. Faulhaber, D. Y. K. Ko, and O. R. Briddon, Phys. Rev. B **48**, 661 (1993).

[5] V. P. Antropov, O. Gunnarsson, and A. I. Liechtenstein, Phys. Rev. B **48**, 7651 (1993).
[6] N. Manini, A. Dal Corso, M. Fabrizio, and E. Tosatti, Philos. Mag. B **81**, 793 (2001).
[7] M. Saito, Phys. Rev. B **65**, 220508 (2002).
[8] O. Gunnarsson, Rev. Mod. Phys. **69**, 575 (1997).
[9] P. B. Allen and B. Mitrovic, in *Solid State Physics*, Vol. 37, edited by H. Ehrenreich, D. Turnball, and F. Seitz (Academic, New York, 1982).
[10] E. Koch, O. Gunnarsson, and R. M. Martin, Phys. Rev. Lett. **83**, 620 (1999).
[11] L. Pietronero, S. Strässler, and C. Grimaldi, Phys. Rev. B **52**, 10516 (1995).
[12] C. Grimaldi, L. Pietronero, and S. Strässler, Phys. Rev. B **52**, 10530 (1995).
[13] C. Grimaldi, L. Pietronero, and S. Strässler, Phys. Rev. Lett. **75**, 1158 (1995).
[14] E. Cappelluti, C. Grimaldi, L. Pietronero, and S. Strässler, Phys. Rev. Lett. **85**, 4771 (2000).
[15] A. B. Migdal, Sov. Phys. JETP **7**, 996 (1958).
[16] R. Zeyher and M. L. Kulić, Phys. Rev. B **53**, 2850 (1996).
[17] M. L. Kulić, Phys. Rep. **338**, 1 (2000).
[18] M. Grilli and C. Castellani, Phys. Rev. B **50**, 16880 (1994).
[19] Z. B. Huang, W. Hanke, E. Arrigoni, and D. J. Scalapino, cond-mat/0306131 (unpublished).
[20] A. Georges, G. Kotliar, W. Krauth, and M. Rozenberg, Rev. Mod. Phys. **68**, 13 (1996).
[21] M. Capone, M. Fabrizio, C. Castellani, and E. Tosatti, Science **296**, 2364 (2002).
[22] J. E. Han, O. Gunnarsson, and V. H. Crespi, Phys. Rev. Lett. **90**, 167006 (2003).
[23] S. Satpathy, V. P. Antropov, O. K. Andersen, O. Jepsen, O. Gunnarsson, and A. I. Liechtenstein, Phys. Rev. B **46**, 1773 (1992).
[24] M.-Z. Huang, Yong-Nian Xu, and W. Y. Ching, Phys. Rev. B **46**, 6572 (1992).
[25] A. M. Panich, H.-M. Vieth, P. K. Ummat, and W. R. Datars, Physica B **327**, 102 (2003).
[26] W. L. Yang *et al.*, Science **300**, 303 (2003).