Correlation effects in the bulk modulus and equilibrium lattice spacing of the transition metals

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CORRELATION EFFECTS IN THE BULK MODULUS AND EQUILIBRIUM LATTICE SPACING OF THE TRANSITION METALS

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Résumé. — Le rôle des corrélations dans le module de rigidité et le paramètre cristallin d'équilibre des métaux de transition est étudié par une méthode de perturbation reliée à l'approximation de Gutzwiller. On trouve qu'il décroît le module de rigidité et accroît le paramètre cristallin ; l'effet est maximum dans le milieu de la série 3d, en accord avec l'expérience.

Abstract. — The role of correlations in the bulk modulus and equilibrium lattice spacing of the transition metals is studied using a perturbation method related to Gutzwiller's approximation and is found to decrease the bulk modulus and increase the lattice spacing, the effect being greatest in the middle of the 3d series in agreement with experiment.

As is seen in figure 1 the bulk modulus in the 4d and 5d transition metal series varies regularly with the filling of the band with a maximum in the middle of the series [1] corresponding to the maximum cohesion found for half filled d bands by Friedel [2]. In the 3d series, however, there is a marked deviation from this behaviour, the bulk modulus of Cr, Mn, Fe and Co being smaller than the values expected from the trend in the 4d and 5d series. A similar anomaly is seen in the equilibrium atomic volume of the 3d series [1] shown in figure 2, the atomic volume of Fe and Co being larger than that of Ni in contrast to the behaviour in the 4d and 5d series where the atomic volume varies regularly with the filling of the d band with a minimum corresponding to a maximum cohesion in the middle of the series. Mn is particularly notable for its large atomic volume and small bulk modulus, and has properties more like Cu in the same period with a full d band than Tc and Re in the same group where the d electrons contribute strongly to the cohesion.

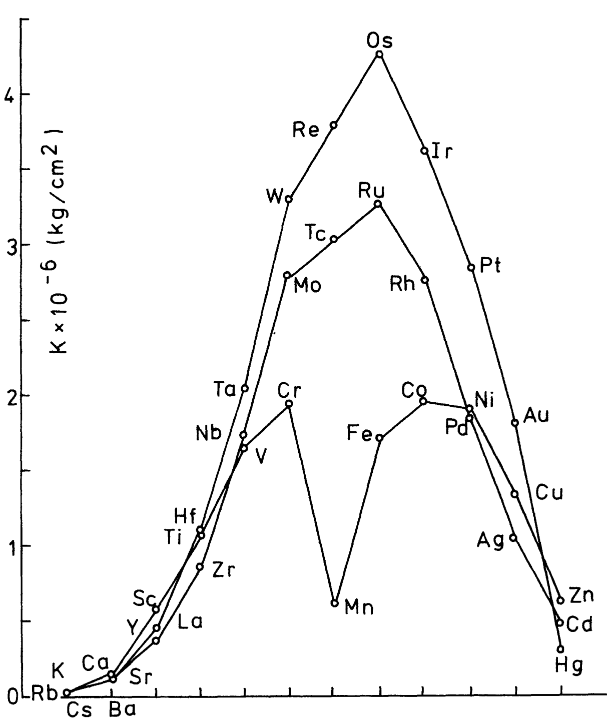

FIG. 1. — Bulk modulus of the transition metals after Gschneider [1].

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We have shown [3] that to second order in the electron-electron interaction energy U, the part of the d electron energy dependent on the bandwidth W is

$$E_B = -AW - B/W \qquad (1)$$

where

$$A = \frac{z}{20}(10 - z)$$

$$B = 45\left[\frac{z}{10}\left(1 - \frac{z}{10}\right)U\right]^2 \qquad (2)$$

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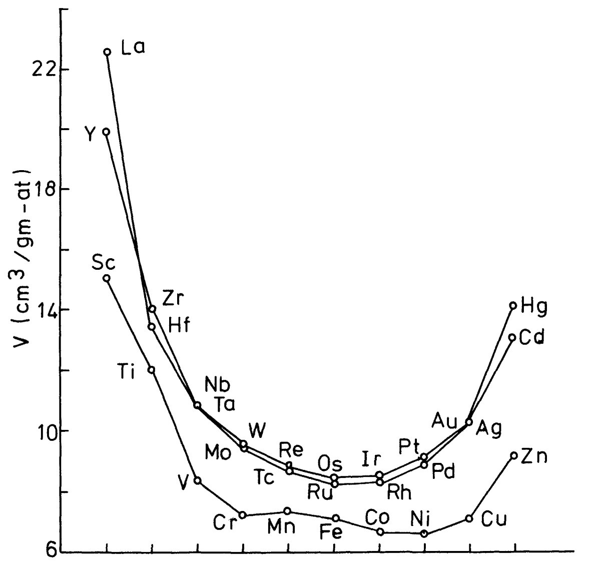

FIG. 2. — Atomic volume of the transition metals after Gschneider [1].

z being the average number of electrons/atom in the d band and where we have assumed five overlapping rectangular d bands for simplicity. The first term in (1) represents the band energy of the d electrons in the absence of correlations and gives good agreement with the measured cohesive energy in the 4d and 5d series [2]. The second term in (1) represents the first order contribution of correlations to the energy and reduces the electron interaction energy $9 z^2 U/20$ in the solid by preventing the electrons hopping on the same atom.

To study the equilibrium atomic volume and bulk modulus it is necessary to introduce a repulsive interaction between atoms, operative at short distances, to prevent the crystal collapsing under the cohesive forces, and following Ducastelle [4], who studied the elastic moduli and atomic radii in the transition metals neglecting correlation effects, we shall use the Born-Mayer form

$$E_R = C\,\mathrm{e}^{-pR} \tag{3}$$

where R is the Wigner-Seitz radius, together with the approximation for the bandwidth

$$W = W_0\,\mathrm{e}^{-qR}\,. \tag{4}$$

Neglecting the correlation correction B/W in (1) we obtain, upon minimising the energy, the equilibrium Wigner-Seitz radius

$$R_0 = \frac{1}{p-q}\ln\frac{pC}{qAW_0} \tag{5}$$

as obtained by Ducastelle [4]. To first order in the correlation we then find for the relative change in the Wigner-Seitz radius due to correlations

$$\alpha \equiv \frac{R-R_0}{R_0} \approx \frac{9}{(p-q)\,R_0}\,\frac{z}{10}\left(1-\frac{z}{10}\right)\frac{U^2}{W^2}\,. \tag{6}$$

The effect of correlations is thus seen to be a lattice expansion, the effect being greatest for a half filled d band (neglecting the dependence of U, W, pR_0 and qR_0 on z).

Taking the value of $pR_0 \approx 6$, $qR_0 \approx 3$ used by Ducastelle [4] and the average values $U \approx 3$ eV, $W \approx 6$ eV deduced for the 3d series [3] we find a 20 % increase in the Wigner-Seitz radius in the middle of the 3d series due to correlation effects which is rather larger than the observed anomaly. Inclusion of higher order terms in the perturbation expansion would act to reduce this correction.

The bulk modulus K is given by

$$K = V\frac{\mathrm{d}^2E}{\mathrm{d}V^2} = \frac{R^2}{9\,V}\,\frac{\mathrm{d}^2E}{\mathrm{d}R^2}\,. \tag{7}$$

Neglecting correlation effects we find, following Ducastelle [4],

$$K_0 = \frac{q(p-q)\,R_0^2}{9\,V}\,AW \approx \frac{AW}{V} \tag{8}$$

using $pR_0 \approx 6$, $qR_0 \approx 3$, which varies parabolically with z in good agreement with the measured values in the 4d and 5d series [4]. The relative change in the bulk modulus β to first order in the correlation is then

$$\begin{aligned}\beta K_0 \equiv K - K_0 &= -\frac{q^2R^2}{V}\,5\left[\frac{z}{10}\left(1-\frac{z}{10}\right)\right]^2\frac{U^2}{W}\\ &\approx -\frac{45}{V}\left[\frac{z}{10}\left(1-\frac{z}{10}\right)\right]^2\frac{U^2}{W}\end{aligned} \tag{9}$$

with $qR \approx 3$.

A very similar expression is obtained using Heine's [5] approximation $W \sim R^{-5}$ which gives upon differentiating the second term in (1) twice

$$\beta K_0 = -\frac{50}{V}\left[\frac{z}{10}\left(1-\frac{z}{10}\right)\right]^2\frac{U^2}{W}\,. \tag{10}$$

Correlation is thus seen to reduce the bulk modulus, the reduction being greatest in the middle of the series. For $z = 5$, $U = 3$ eV and $W = 6$ eV, this reduction is of the order of 50-60 % and is in good agreement with the magnitude of the anomaly observed in the 3d series. Values deduced for U and W for the 4d and 5d series [3] lead to nearly negligible corrections α and β.

In a complete treatment the occurrence of magnetism in the second half of the 3d series should also be included. We shall not discuss here the antiferromagnetism of Cr and Mn but only the ferromagnetism of Fe, Co and Ni. We have shown [3] that in the ferromagnetic state with $(z + \mu)/2$ electrons per atom having spin ↑ and $(z - \mu)/2$ having spin ↓ that A and B transform to become

$$A = \frac{z}{20}(10 - z) - \frac{\mu^2}{20}$$

$$B = 45\left[\frac{z}{10}\left(1 - \frac{z}{10}\right) U\right]^2 + [-1 - 0.14\, z(10 - z) + 0.09\,\mu^2]\, U^2 \frac{\mu^2}{20}.$$

Eq. (11) has been derived for the case of five overlapping rectangular bands [3] and holds for all values of μ^2. The term in μ^4 has been shown [3] to be important in determining the stability of ferromagnetism and arises from the change in phase space available for electron-electron scattering upon magnetization. This term is known to be necessary in the itinerant model of ferromagnetism in order to obtain agreement with the observed magnetization *versus* temperature curves [6].

Using (11) the effect of magnetization on the Wigner-Seitz radius and bulk modulus may be investigated. Neglecting the correlation correction B/W, R_0 transforms such that

$$\frac{\delta R_0}{R_0} = -\frac{1}{(p - q)\, R_0} \ln\left[\frac{z(10 - z) - \mu^2}{z(10 - z)}\right] \quad (12)$$

where, for a strong ferromagnet at the end of the series such as Co or Ni, $\mu = (10 - z)$.

Similarly neglecting correlation effects the change in the bulk modulus due to magnetization is

$$\frac{\delta K_0}{K_0} = -\frac{\mu^2}{z(10 - z)}. \quad (13)$$

In addition magnetization reduces the correlation corrections α and β to R and K by reducing the number of interactions between electrons of opposite spin. Table I compares the correlation corrections α_{μ^2} and β_{μ^2} in the magnetic state with those in the non-magnetic state α_{NM} and β_{NM} given by (6) and (9), and with the corrections to R_0 and K_0 due to magnetization in the absence of correlations given by (12) and (13). Both magnetization and correlation act to decrease the bulk modulus and increase the Wigner-Seitz radius due to the transfer of electrons into orbitals of high kinetic energy, the effect of magnetization being rather smaller than that of correlation.

TABLE I

Comparison of the effect of correlation and ferro-magnetization on the Wigner-Seitz radius and bulk modulus of Fe, Co *and* Ni.

	Fe	Co	Ni
z	7.1	8.3	9.4
μ	2.2	1.7	0.6
α_{NM}	0.154	0.106	0.042
α_{μ^2}	0.114	0.075	0.035
$\delta R_0/R_0$	0.089	0.076	0.022
β_{NM}	− 0.463	− 0.317	− 0.127
β_{μ^2}	− 0.341	− 0.224	− 0.106
$\delta K_0/K_0$	− 0.235	− 0.205	− 0.064

In conclusion, correlation effects are found to have their maximum effect for a half filled d band and are responsible to a large extent [7] for the anomaly in the behaviour of the bulk modulus and Wigner-Seitz radius observed in the 3d transition metal series.

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