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Effect of correlation on the band structure of cerium

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Abstract. The electronic band structure of f.c.c. phase of the rare earth metal cerium (α-cerium) has been calculated using a formulation of the crystal potential where correlation also has been included in addition to exchange. We use the prescription of Cohn and Sham as well as that of Overhauser. The Green's function method of Korringa-Kohn and Rostoker has been used for obvious advantages in the calculation. The calculations indicate that the s–d bands are hybridized with the f-levels but the f-bands are fairly narrow and lie slightly above the Fermi level. The structure of the bands is qualitatively similar to those of calculations by others except for a general shift of the entire set of bands by about 0·1 Ryd. The density of states has been calculated from the bands obtained. The spin susceptibility of α-cerium has also been calculated using the Kohn–Sham method. However, the calculated additional contributions to the band structure values cannot still explain the large experimental values reported in the literature.

Keywords. Energy bands; rare earth metals; cerium; density of states; KKR method; spin susceptibility.

1. Introduction

The electronic band structure and the Fermi surface of metallic cerium (Ce) have recently been calculated by the APW method (Mukhopadhyay and Majumdar 1969, Mukhopadhyay 1972). The unusual physical properties exhibited by this metal in f.c.c. phase have attracted much attention and have been reviewed several times (Gschneidner 1965, Coqblin and Blandin 1968, Mukhopadhyay 1973).

In Mukhopadhyay's calculation, the effect of changing the exchange potential from Slater (1951) value 1 to the Kohn-Sham-Gàspàr (Kohn and Sham 1965, Gàspàr 1954) value 2/3 is thoroughly investigated. It is found that the f-band is very sensitive to the exchange potential, but the remaining structure is not. For the Slater exchange the f-band lies well below the s-d conduction bands; it rises quickly as the exchange coefficient is reduced and at the value 2/3 the f-band lies above the Fermi level. The Kohn-Sham formulation of the band structure problem has not only the 2/3 value for the exchange, but also shows how a part of the potential comes from the correlation energy. This has not been included in any previous calculation, although a rough idea of what might happen can be gained from changing the coefficient of the exchange term. In this brief paper we want to present the results of a computation that includes the correlation potential.

It is well known that the correlation energy for actual metallic densities $2 \leq r_s \leq 6$ cannot be rigorously computed, r_s being the standard electron gas parameter of inverse density. Usually we have to use interpolation formulas between the computations strictly valid at small r_s and at large r_s. Several interpolation formulas are possible each leading to a different potential. In order to have flexibility in this regard, it is convenient to use the Green's function or KKR method (Korringa 1947, Kohn and Rostoker 1954) rather than the APW method, because in the KKR method, a clear separation between the kinematical and dynamical parts exists and it is not necessary to repeat the kinematical part of the computation for a different potential. We have adapted the published Green's function programme—that by Faulkner *et al.* (1967)—on a CDC 3600 computer for this purpose.

In the next section we discuss the potential used and then describe the results obtained in section 3. In section 4 we give the results on calculated spin paramagnetic susceptibility.

2. Construction of the potential

The details of the Green's function method are well known (Singh 1968) and need no repetition. We shall simply describe the construction of our potential.

We follow Mukhopadhyay (1973) for the direct atomic potential in the following manner. This contains the nuclear part $-2Z/r$ in rydbergs and the direct Coulomb part obtained from atomic charge density of Liberman *et al* (1965). The effects of potentials due to neighbouring atoms around the central atom chosen as origin are obtained by α-expansion technique of Löwdin (1956) as discussed by Loucks (1967). To this we must add $\mu_{xc}[n(r)]$ given by Kohn and Sham (1965) of the form

$$\mu_{xc}[n] = \frac{d}{dn}[n\epsilon_{xc}(n)] \tag{1}$$

where $\epsilon_{xc}(n)$ is the exchange and correlation energy per electron of a uniform electron gas of density n. For the exchange part only we get

$$\mu_x(r) = -\frac{1}{\pi}(3\pi^2 n(r))^{1/3} \tag{2}$$

in atomic units or

$$\mu_x(r) = -\frac{2}{\pi}(3\pi^2 n(r))^{1/3}\ \text{Ryd} \tag{3}$$

which is the usual KSG exchange part. For correlation energy we shall use the old Wigner (1938) interpolation

$$\epsilon_c = -\frac{0\cdot 88}{r_c + 7\cdot 8}\ \text{Ryd} \tag{4}$$

so that

$$\epsilon_c = -\frac{0\cdot 88}{C_0 n^{-1/3} + 7\cdot 8} \tag{5}$$

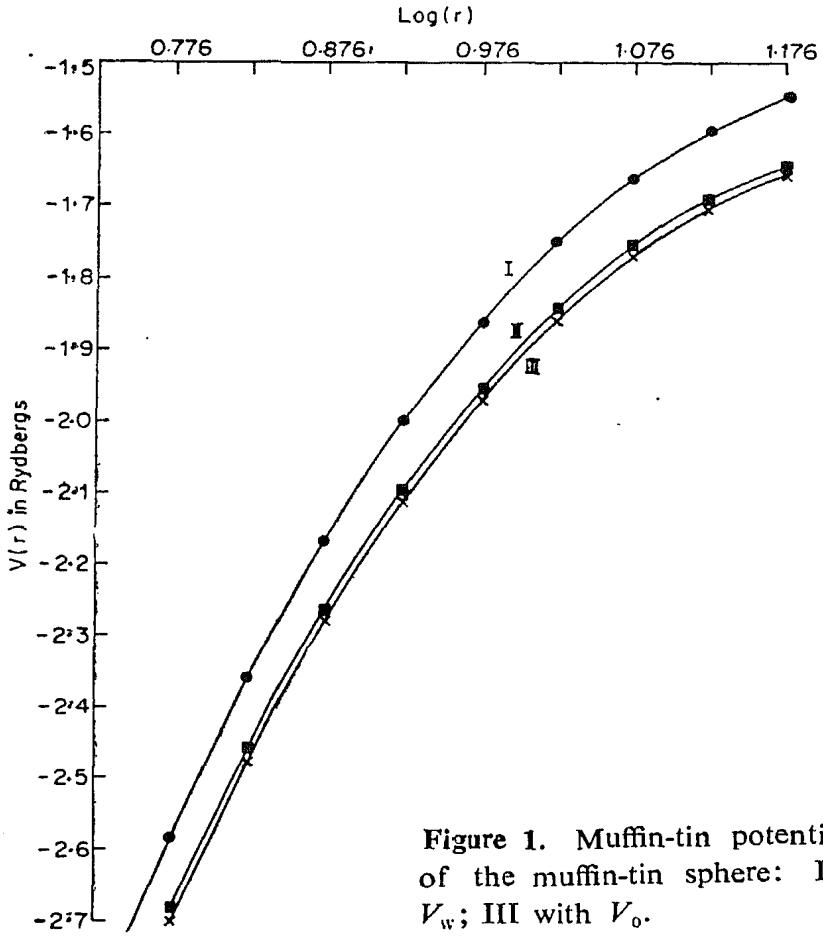

Figure 1. Muffin-tin potential for α-cerium near the boundary of the muffin-tin sphere: I with KSG–exchange; II with V_w; III with V_0.

$$C_0 = \left(\frac{3}{4\pi}\right)^{1/3} = 0\cdot 62.$$

The correlation part of the potential comes out to be

$$\mu_c(r) = -\frac{0\cdot 88\, n(r)^{1/3}}{0\cdot 62 + 7\cdot 8\, n(r)^{1/3}}\left[1 + \frac{1}{3 + 37\cdot 72\, n(r)^{1/3}}\right] \tag{6}$$

and the total exchange and correlation potential becomes

$$V_w(r) = -\frac{2}{\pi}\left(3\pi^2 n(r)\right)^{1/3} - \frac{0\cdot 88\, n(r)^{1/3}}{0\cdot 62 + 7\cdot 8\, n(r)^{1/3}}\left[1 + \frac{1}{3 + 37\cdot 72\, n(r)^{1/3}}\right]. \tag{7}$$

Since the other correlation formulas give very similar results we believe that V_w is perhaps typical of all of them. Recently, Overhauser (1971) has proposed a very simple exchange and correlation potential

$$A_{xc} = -2\cdot 07\,(na_0^3)^{0\cdot 3}\ \text{Ryd} \tag{8}$$

where a_0 is the Bohr radius and the electron density n is expressed in a_0^{-3} units. In our units it is

$$V_0(r) = -2\cdot 07\,(n(r))^{0\cdot 3}\ \text{Ryd}. \tag{9}$$

The significant thing about this potential is that the power of n is not 1/3 but 0·3.

The relative difference of the two complete potentials is appreciable only at the extremities of the cell. Figure 1 shows a plot of these potentials, as well as the one constructed without correlation energy.

3. Results on the calculated band structure

We present in figures 2 and 3 the results of our calculation of the band structure of α-cerium. The structure is qualitatively similar to previous results of Mukhopadhyay (1972) using APW method, except for a general shift of the entire set of bands by about 0·1 Ryd caused by the greater attractive nature of the potentials used by us. The s-d bands are hybridized with the f-levels, but we obtain a fairly narrow group of f-bands lying slightly above the Fermi level, no matter whether we allow three or four conduction electrons. This picture supports the qualitative features of the Ramirez-Falicov (1971) model for α-γ transformation in cerium.

For the case of V_w, the band structure is remarkably close to that of the ordinary, KSG potential. In the case of V_0, the level Γ'_{25} comes down below Γ'_2 and the entire f-band levels Γ'_2, Γ_{15}, Γ_{25} lie between Γ'_{25} and Γ_{12}. The narrow bands spread more than the V_w case almost 3/2 times. The qualitative features are reproduced correctly. Since Overhauser's potential has a different power behaviour this is a heartening feature.

The density of states $\mathcal{D}(E_F)$ of α-cerium for the V_w or V_0 choice of exchange-correlation potentials are presented in figures 4 and 5. For the three conduction

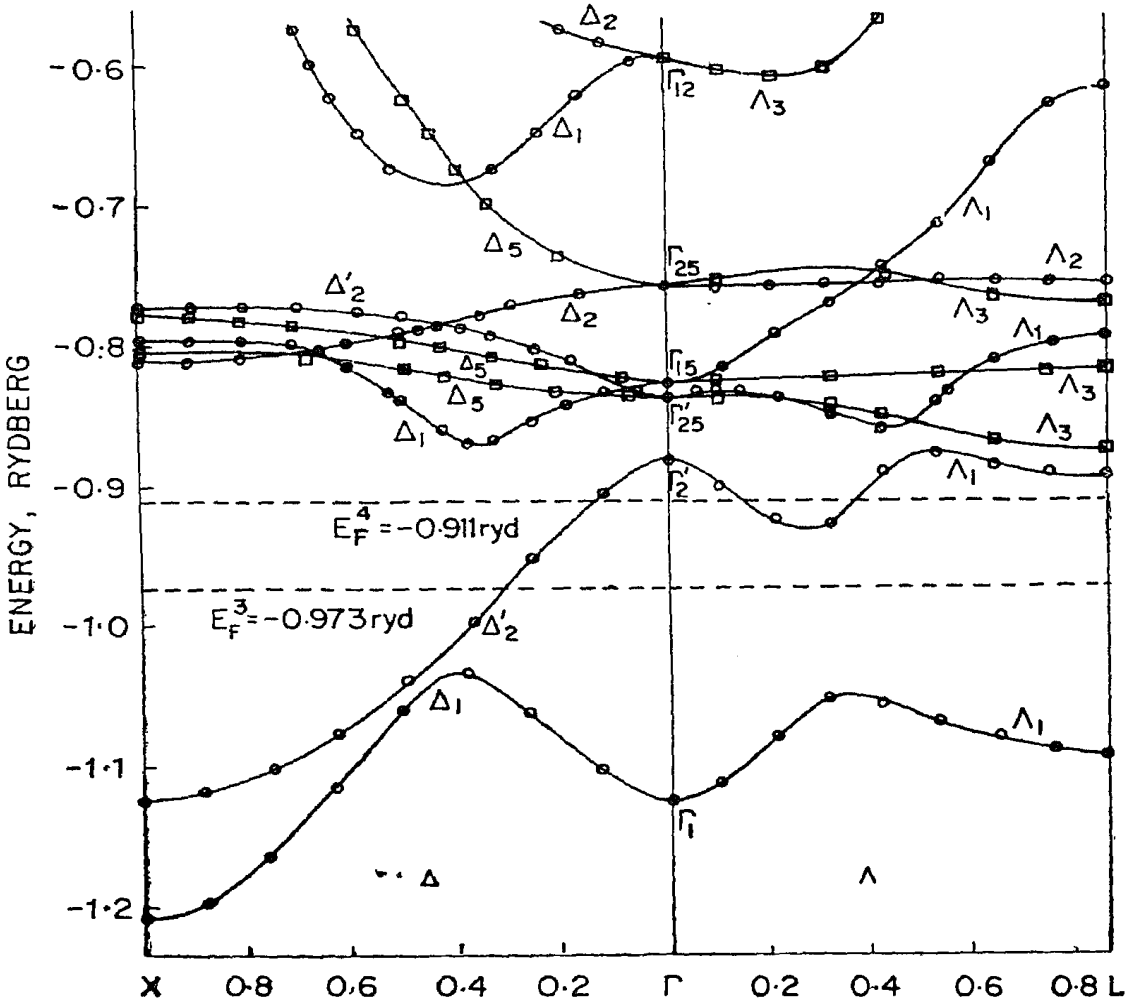

Figure 2. Band structure of α-cerium for the crystal potential with V_w. The broken lines show the positions of the Fermi levels with 3 and 4 conduction electrons per atom. The curves along which the points plotted are indicated by squares represent doubly degenerate bands.

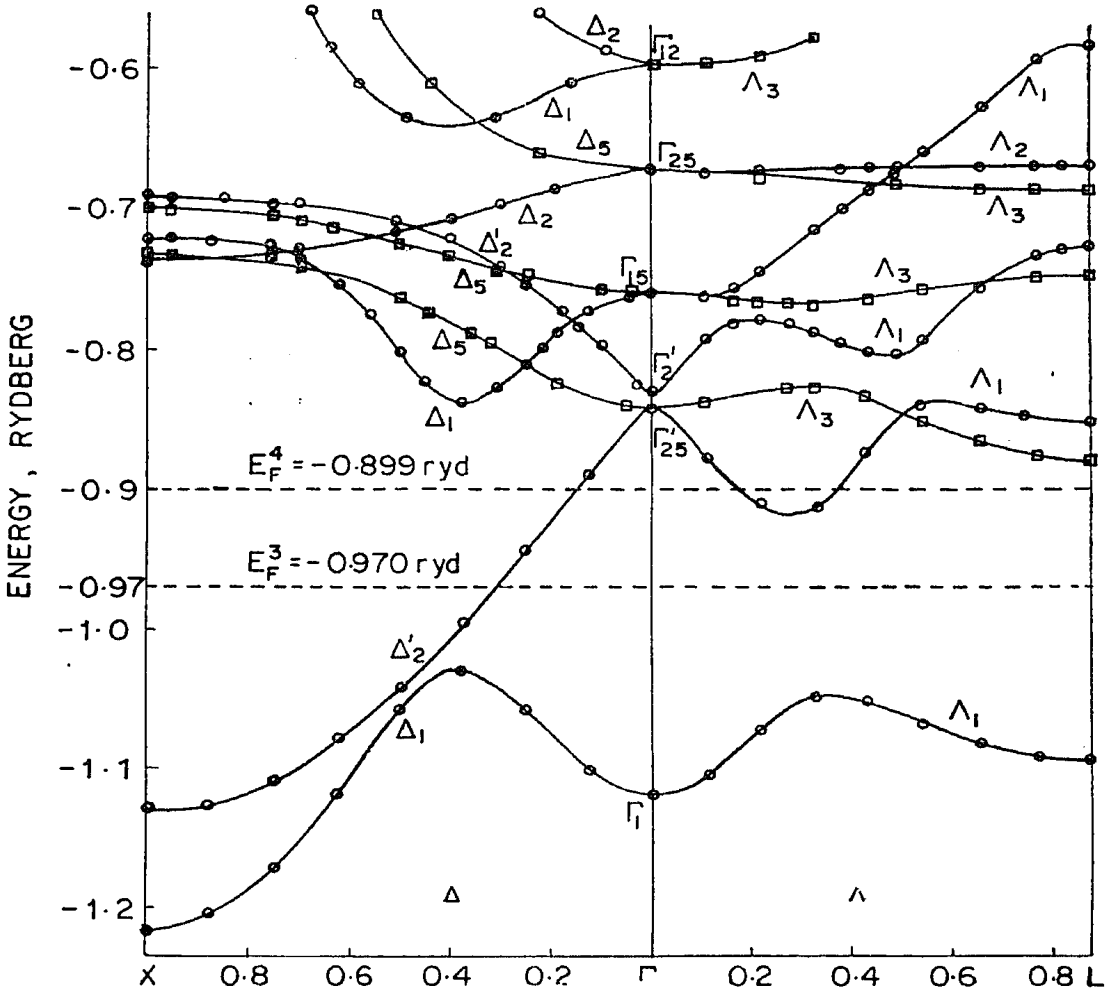

Figure 3. Band structure of α-cerium for the crystal potential with V_0. The broken lines show the positions of the Fermi levels. Square points correspond to doubly degenerate bands.

electron case the values at the Fermi energy are 2·06 and 1·91 electrons/(atom. eV) respectively and for the four-conduction-electron case the values are smaller. These are 1·06 and 0·98 electrons per atom per electron volt respectively. These values of density of states and their trends are similar to earlier computations.

4 Spin paramagnetic susceptibility

It is possible to calculate the spin paramagnetic susceptibility of α-cerium using the Kohn-Sham (1965) method. The magnetic behaviour of cerium metal is extremely complicated but it is known that α-cerium shows essentially, a weakly temperature-dependent Pauli paramagnetism (MacPherson *et al* 1971) and that the susceptibility in units of electrons/(atom.eV) is 20·3 (Grimberg *et al* 1971, 1972). This is unusually large. The above result implies that the effective density of states is 20·3 electrons/(atom.eV) if we represent the measured suceptibility the usual electron gas formula $\mu_B^2 \mathcal{D}(E_F)$.

The Kohn-Sham expression for the susceptibility is

$$\chi = \chi_s + \frac{1}{V}\int \{\chi_1[n(\boldsymbol{r})] - \chi_0[n(\boldsymbol{r})]\}\, d^3\boldsymbol{r} \tag{10}$$

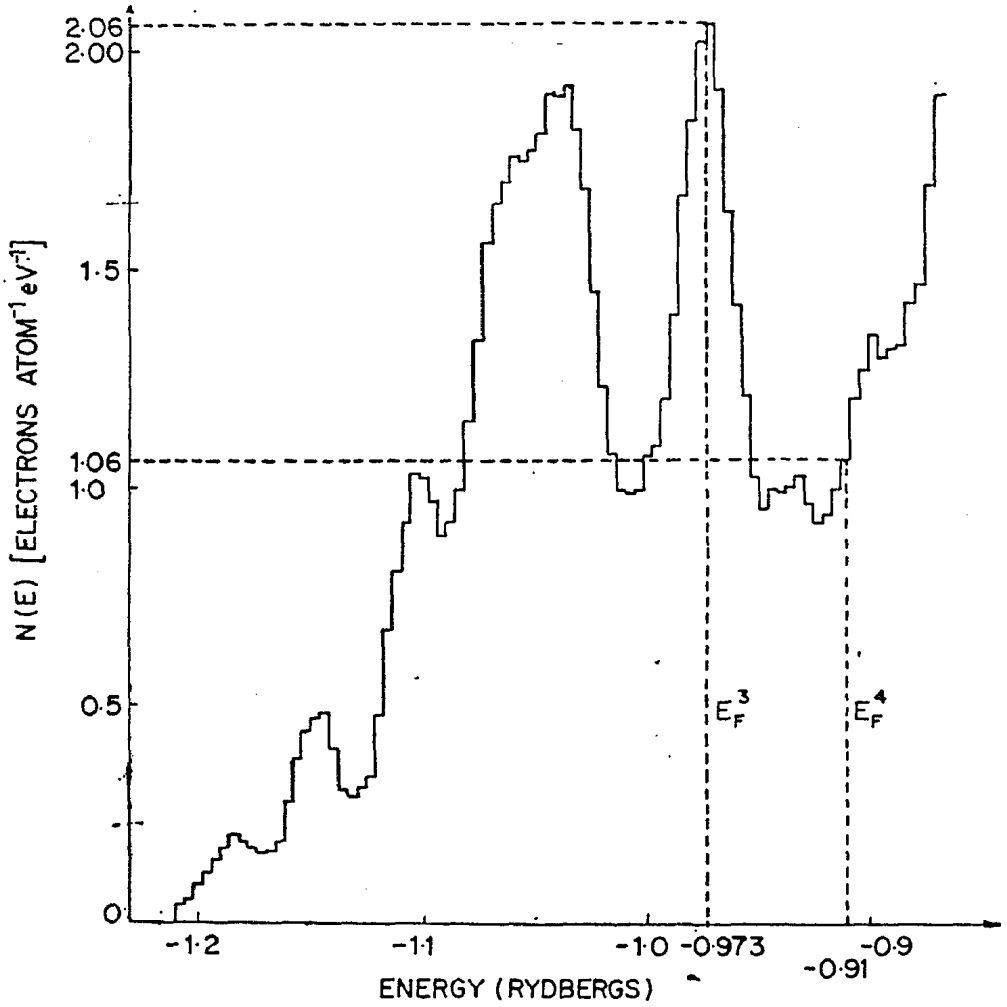

Figure 4. Density of states $N(E)$ for α-cerium for the case of V_{11}. E_F^n $(n = 3, 4)$ indicates the position of the Fermi level with n electrons per atom in the conduction band.

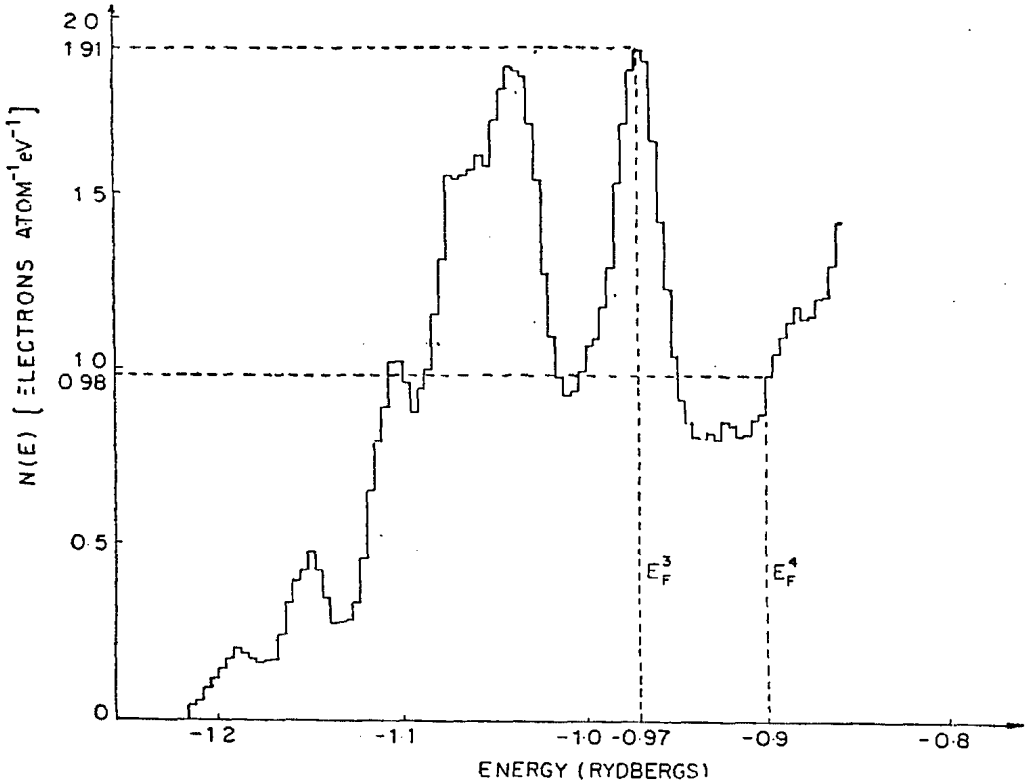

Figure 5. Density of states $N(E)$ for α-cerium for the case of V_Q. E_F^n $(n = 3, 4)$ indicates the position of the Fermi level with n electrons per atom in the conduction band.

Here χ_s is the Pauli susceptibility while $\chi_i(n)$ and $\chi_0(n)$ are the respective susceptibilities for a uniform system with and without interaction.

According to Mukhopadhyay's (1973) APW calculations with 3 and 4 electrons, the susceptibility χ_s is 1·53 and 1·18 electrons/(atom.eV) respectively (Liberman's data for charge density). With correlation included, for three electrons in the conduction band $V_w(r)$ gives 2·06 and $V_0(r)$ gives 1·91. For four electrons the respective values are 1·06 and 0·98. There is one piece of evidence that indicates these values to be fair. This is the experimentally determined density of states from electronic specific heat measurements which comes out to be 4·15 electrons/(atom.eV). Mukhopadhyay and Gyorffy (1973) have estimated the phonon enhancement λ to be 0·87 for trivalent α-cerium and 1·11 for the tetravalent one (Liberman's data). Thus the corrected density of states are 2·22 and 1·97 respectively. For the trivalent case, the inclusion of correlation improves the agreement, but not for the tetravalent case. Since one cannot assign strict valency to metallic α-cerium and the λ values are also somewhat uncertain, we could say that the density of states is of the correct order of magnitude.

In order to calculate the additional contribution to susceptibility as in (10), we face the difficulty that χ_i for the interacting uniform system is not known. Using approximate formulas for χ_i we may estimate the additional contribution as follows:

The Hartree-Fock susceptibility for the uniform gas is

$$\chi_{HF} = \frac{\chi_0}{1 - (0\cdot 103/n^{1/3})} \tag{11}$$

where

$$\chi_0 = \mu_B^2 \mathcal{D}(E_F) = \mu_B^2 \left\{ \frac{a_L^3}{8\pi} \left(\frac{3}{\pi}\right)^{1/3} \frac{n^{1/3}}{13\cdot 61} \right\}$$

electrons/(atom.eV), a_L being the lattice constant. We take for $n(\boldsymbol{r})$ the charge density used for the band structure calculations and computed from Liberman's data. The unit cell is replaced by Wigner-Seitz sphere and we retain only the spherically symmetric component of the charge density. This leads to the additional contributions

$$\chi_{add} = \frac{2}{13\cdot 61\pi^2} \int_0^{r_{ws}} \frac{r^2\,dr}{1 - [0\cdot 103/n(r)^{1/3}]}$$

$$= 0\cdot 341 \text{ electron/(atom.eV)} \tag{12}$$

where r_{ws} is the radius of the Wigner-Seitz sphere. Instead of (11) we may use the Brueckner-Sawada (1958) formula for the susceptibility of an interacting uniform electron gas.

$$\chi = \frac{\chi_0}{1 - (0\cdot 103/n^{1/3}) + (0\cdot 00529/n^{2/3})\,\{1\cdot 534 - \ln(0\cdot 103/n^{1/3})\}}. \tag{13}$$

The additional contribution is in fact smaller, only 0·16 electron/(atom.eV). In any case the total susceptibility falls far short of the experimental value. It is worthwhile to note that the contributions (11) or (13) are independent of what exchange or correlation we use, this being due to our choice of $n(\boldsymbol{r})$. If one were

to use the $n(\boldsymbol{r})$ computed from the band structure wavefunctions, this contribution will change. But this is not likely to resolve the disagreement with experiment which is still large.

We ought to note that (11) and (13) are derived for uniform electron gas theories and they are not strictly applicable to interacting inner core electrons. If one argues that only the outer electrons should be counted in using (11) and (13) one gets corrections to be somewhat larger but not appreciably so much as to be able to explain experimental results.

Clearly the susceptibility of α-cerium remains unexplained in this way of computation, partly because equations (11) and (13) are inadequate. We would, however, like to mention that in the literature (Herring 1966) instead of χ, more often its inverse is computed. One could obtain an equation for χ^{-1} analogous to (10) and preliminary estimates seem to be encouraging. We hope to return to this problem later.

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