PHYSICAL REVIEW B VOLUME 3, NUMBER 8 15 APRIL 1971

Theory of the α-γ Phase Transition in Metallic Cerium

Ricardo Ramirez* and L. M. Falicov
Department of Physics, † *University of California, Berkeley, California* 94720
(Received 29 June 1970)

A simple model for the α-γ phase transition in Ce is presented. It is based on the change of occupation number of the f levels, which are assumed to be atomiclike in character, i.e., highly correlated and with a very narrow bandwidth. The change in occupation number is, as a function of temperature, caused by the short-range part of the electron-electron interaction. The theory allows for the existence of a critical point. With the assumption of a linear relationship between f-level occupation numbers and lattice constant, pressure–lattice-constant isotherms are calculated. Curves for the paramagnetic susceptibility as a function of pressure and temperature are also presented.

I. INTRODUCTION

The properties of rare-earth metals can usually be explained by an s-f exchange interaction between a free trivalent ion and the conduction electrons. One exception is cerium which presents a more complex behavior. Its phase diagram[1] is shown in Fig. 1. One can note several solid phases: one bcc phase (δ), one double hexagonal phase (β), two fcc phases (α and γ), and one other closed-packed structure (α') which is either cubic[1,2] or hexagonal.[3] In this paper, we are only concerned with the α and γ phases. The experimental information with regard to these two phases can be summarized as follows[4–6]: (a) Both α and γ phases are cubic closed packed[7] (fcc); (b) the γ phase is magnetic while the α phase is not[8]; (c) the atomic radius of the γ phase is very similar to the radii of its neighbors lantanum and praseodymium; the radius of the α phase is, however, smaller[9]; (d) from Hall-effect measurements, it has been estimated[10] that the valency of the γ and α phases are 3.06 and 3.67, respectively; (e) at room temperature the lattice constant changes discontinuously at about 7 kbar from 5.16 Å for the γ phase to 4.85 Å for the α phase[2]; and (f) the first-order phase-transition line between the α and γ phases ends up[4,11–13] in a critical point C corresponding to $p_C \cong 17.5$–20 kbar and $T_C \cong 550$–630 °K; this critical point is in all respects similar to a liquid-gas critical point and, by properly choosing a path in the p-T diagram it is possible to go continuously from a large-spacing magnetic γ phase to a more dense nonmagnetic α phase.

Several theories have been proposed to explain such a fascinating behavior of Ce metal. The simplest arguments, based on chemical considerations,[14,15] suggest the promotion of one electron from an f orbital in the γ phase to an s-d hybridized conduction-band orbital in the α phase. In this way, the α phase consists of Ce^{4+} ion cores and four conduction electrons per atom; the Ce^{4+} core, isoelectronic with the Xe atom, is nonmagnetic ($J=0$). On the other hand, the γ phase is formed by a set of Ce^{3+} ion cores and three conduction electrons per atom; the Ce^{3+} ion has a well-defined magnetic moment[16] corresponding to $J=\frac{5}{2}$ and a g factor $g=0.811$. These properties are in agreement with the experimental facts.

The detailed mechanisms for the promotion of the relevant electron and the consequent phase transition are however not completely clear. Blandin and co-workers[4,5] have proposed a model based on the hybridization of the f shell and the conduction band, together with a strong spin-orbit interaction. Their model explains the existence of a critical point and is based on localized f-like energy levels whose energies (with respect to the Fermi level) are strong functions of temperature and pressure. The nature of and the reason for those strong dependences are, however, not given explicitly in the paper. In addition the existence of a first-order phase transition depends crucially on the orbital degeneracy of the f states.

All these models and speculations (and the model here presented as well) are based on the simultaneous existence of localized or almost localized f states, and itinerant conduction electron states, derived from hybridized s and d bands. This concept, although not a common one among solid-state (band) theorists, is not a new one. When calculating band structures for rare earths and actinides by the augmented-plane-wave method,[17,18] most authors[19] do not include the $l=3$ (f-states) contributions; if included, they usually spoil the beautiful agreement between theoretical and experimental data on the Fermi surface of these materials. The $l=3$ solutions are, however, there and their energies are quite similar to conduction-band energies, most times overlapping the conduction band. Justification for the omission can be based on the fact that the $l=3$ states have a very narrow bandwidth and should therefore be highly correlated states, i.e., states which will approximate the localized picture envisioned by Mott[20] in the insulating limit of the

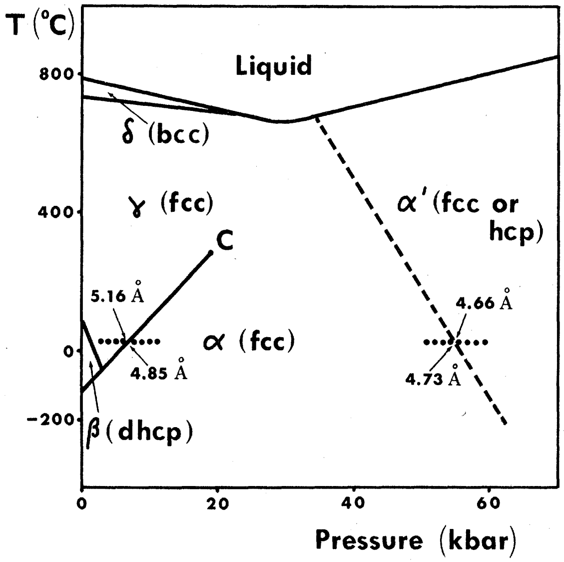

FIG. 1. Phase diagram of Ce. The values in Å represent the lattice constants at the transition point at room temperature. C is the critical point (after Refs. 1–3).

metal-insulator transition systems.

The model we present here also involves both localized f states and itinerant conduction-band states; the mechanism for the α-γ phase transition is, however, due to the short-range part of the electron-electron interaction, more specifically the electron-electron matrix element between f states and conduction-band states. It is quite similar to a model proposed earlier for metal-insulator transitions.[21,22] The details of the model are presented in Sec. II and its physical implications discussed in Sec. III.

II. MODEL

We assume two different types of electron states: (a) an extended band, obtained from hybridized s- and d-like Bloch states. Since these states are 12 per atom in number, and from theory[18] and experiment[23] the fcc rare earths have a density of states of about 20 states/Ry atom, we have assumed, for the sake of simplicity, a conduction band with a constant density of states[24] equal to that value and a total bandwidth $W = 0.6$ Ry $= 8.16$ eV. If in addition we assume that in the α phase at $T = 0$ there are four electrons per atom in the conduction band, and energies are measured from the Fermi energy

$$\epsilon_F = 0 , \tag{2.1}$$

then the conduction bands extend from

$$-W_h = -2.72 \text{ eV} \tag{2.2}$$

to

$$W_e = 5.44 \text{ eV}. \tag{2.3}$$

(b) There is a set of localized f-like states, with an energy E (measured again from $\epsilon_F = 0$), such that $E > 0$. These states, being highly localized and correlated states, admit only one electron per atom. The energy necessary to place a second electron in the same localized f state is at least one order of magnitude larger than E, and for our purposes it can be considered to be infinite.

A schematic diagram of the density of states of this model is shown in Fig. 2. If we take as a reference the state depicted in Fig. 2, the quasiparticle excitations of the system are of three classes: (a) electron excitations in the conduction band, with energies $0 \leqq \epsilon \leqq W_e = 5.44$ eV; (b) hole excitations in the conduction band, with energies $0 \leqq \epsilon \leqq W_h = 2.72$ eV; and (c) localized electrons in the f shell, with energy $\epsilon = E$.

If our crystal contains N atoms, and $n_e(\epsilon)$, $n_h(\epsilon)$, and n_c are the occupation probability of conduction electrons, conduction holes, and localized electrons, respectively, we can write the following relations:

$$N n_a \equiv \int_0^{W_e} D(\epsilon)\, n_e(\epsilon)\, d\epsilon , \tag{2.4}$$

$$N n_b \equiv \int_0^{W_h} D(\epsilon)\, n_h(\epsilon)\, d\epsilon , \tag{2.5}$$

and

$$n_c = n_b - n_a . \tag{2.6}$$

In these equations, $N n_c$ is the number of occupied f levels, $D(\epsilon)$ is the density-of-state function,[24] which in our model is

$$D(\epsilon) = 12N/W , \tag{2.7}$$

and (2.6) is simply the constraint which keeps the number of electrons in the crystal constant.

The excitation energy $\mathcal{E}$ of a given many-electron state consists of two terms

$$\mathcal{E} = \mathcal{E}_1 + \mathcal{E}_2 , \tag{2.8}$$

where $\mathcal{E}_1$ is the single-quasiparticle contribution and $\mathcal{E}_2$ is the quasiparticle-quasiparticle interaction

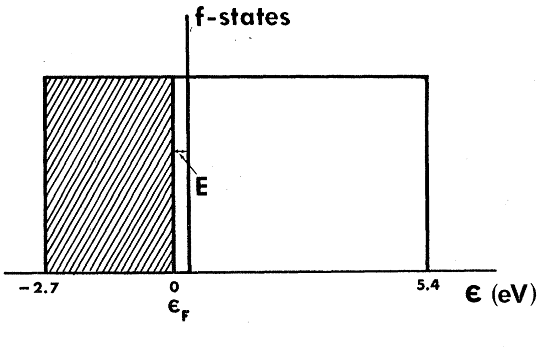

FIG. 2. Density of states for localized electrons and itinerant holes and electrons, as used in the present work.

term.

The term $\mathcal{E}_1$ can be easily written as

$$\mathcal{E}_1=\int_0^{W_e}\epsilon\,D(\epsilon)\,n_e(\epsilon)\,d\epsilon+\int_0^{W_h}\epsilon\,D(\epsilon)\,n_h(\epsilon)\,d\epsilon+NE\,n_c\ . \tag{2.9}$$

In order to write $\mathcal{E}_2$ we make now the following assumptions about the interactions:

(i) All interactions are short range, i.e., only nonzero for electrons which are in the same crystal cell.

(ii) Interaction between two electrons in f levels in the same atom is considered to be infinitely large; exact account is taken of this interaction by not allowing more than one electron per atom in localized states.

(iii) The interaction between electrons in the f shell and either electrons or holes in the conduction band is assumed to be, except for the sign (positive for electrons, negative for holes), constant and independent of ϵ. We denote the value of that interaction (between an electron in the f shell and a hole in a Wannier orbital) by $-G$.

(iv) Interactions between any two quasiparticles in the conduction band are neglected.

With this assumption $\mathcal{E}_2$ can be written as

$$\mathcal{E}_2=-NGn_c(n_b-n_a) \tag{2.10}$$

or, using (2.6),

$$\mathcal{E}_2=-NGn_c^2\ . \tag{2.11}$$

Another way of looking at the interaction G is the following: If we denote by ϵ the energy of one isolated electron moving in a lattice whose potential is set up by a collection of Ce^{4+} ions and a neutralizing charge, the same electron, with the same quantum numbers, would have an energy $\epsilon+G$ when moving in the same lattice but with a potential determined by a collection of Ce^{3+} ions and the corresponding neutralizing charge.

The equilibrium values of the occupation functions $N_e(\epsilon)$, $n_h(\epsilon)$, and n_c are obtained by writing down the free energy $\mathcal{F}$ of the system

$$\mathcal{F}=\mathcal{E}-T\,\mathcal{S} \tag{2.12}$$

at a given temperature T as a function of n_e, n_h, and n_c, and minimizing the whole expression with respect to them. In (2.12) the entropy function is given by

$$\begin{aligned}\mathcal{S}=&-k_B\int_0^{W_e}D(\epsilon)\{n_e(\epsilon)\ln n_e(\epsilon)\\&\qquad+[1-n_e(\epsilon)]\ln[1-n_e(\epsilon)]\}\,d\epsilon\\&-k_B\int_0^{W_h}D(\epsilon)\{n_h(\epsilon)\ln n_h(\epsilon)\\&\qquad+[1-n_h(\epsilon)]\ln[1-n_h(\epsilon)]\}\,d\epsilon\\&-Nk_B\,[n_c\ln n_c+(1-n_c)\ln(1-n_c)]\\&\qquad+Nk_B\,n_c\ln(2J+1)\ ,\end{aligned} \tag{2.13}$$

where k_B is the Boltzmann factor and the four terms in (2.13) correspond to the itinerant-electron entropy, the itinerant-hole entropy, the localized-electron entropy, and the ionic-spin entropy, respectively. In the last term in (2.13),

$$2J+1=6$$

is the spin degeneracy of Ce^{3+}.

When (2.13), (2.8), (2.9), and (2.11) are replaced in (2.12), and (2.12) is minimized with respect to n_e, n_h, and n_c, keeping the constraint (2.4)–(2.6) into account (Lagrange multipliers are used here, as usual), the following results are obtained:

$$n_e(\epsilon)=\{a^{-1}\exp[(\epsilon-E+2Gn_c)/k_BT]+1\}^{-1}\ , \tag{2.14}$$

$$n_h(\epsilon)=\{a\exp[(\epsilon+E-2Gn_c)/k_BT]+1\}^{-1}\ , \tag{2.15}$$

where

$$a\equiv n_c/(2J+1)\,(1-n_c) \tag{2.16}$$

and

$$n_c=\frac{12k_BT}{W}\ln\left|\frac{A_1+e^{-Q_1}}{A_0+e^{-Q_0}}\;\frac{A_0+1}{A_1+1}\right|\ , \tag{2.17}$$

where

$$A_0=1/A_1\equiv a\exp[(E-2Gn_c)/k_BT]\ , \tag{2.18}$$

$$Q_0\equiv W_h/k_BT\ , \tag{2.19}$$

$$Q_1\equiv W_e/k_BT\ . \tag{2.20}$$

Equation (2.17) is an implicit equation for the equilibrium value of n_c as a function of the temperature; it depends on the parameters of the system: W_e, W_h, E, G, and J. For a given temperature T, (2.17) may yield one or three solutions. In the latter case one solution corresponds to a maximum of $\mathcal{F}$ and the other two, to two local minima. In such a case it is necessary to calculate $\mathcal{F}$ numerically in order to determine which one of these two values corresponds to the absolute minimum of $\mathcal{F}$.

Three examples are shown in Figs. 3–5. In all three $W_e=5.44$ eV, $W_h=2.72$ eV, $G=0.44$ eV, and $J=\frac{5}{2}$. In Fig. 3 $E=0.16$ eV and n_c varies discontinuously as a function of T; the discontinuity takes place at $T=382$ °K. In Fig. 4 (critical behavior) $E=0.1894$ eV and n_c varies continuously but has an infinite slope at $T_c=579$ °K. In Fig. 5 $E=0.21$ eV and both n_c and its temperature derivative are continuous.

Before applying the present model to Ce metal, several possible ways of improving it come to mind:

(a) A more realistic density-of-state function $D(\epsilon)$ can be used.

(b) An hybridization term, mixing f and conduc-

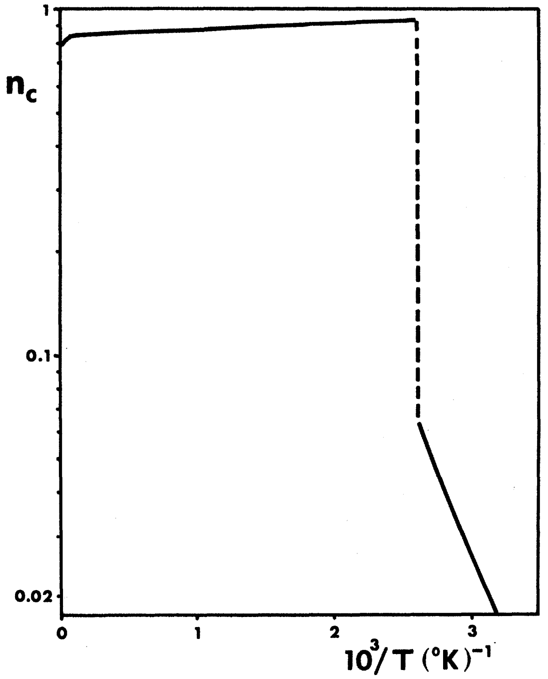

FIG. 3. Plot of n_c as a function of $1000/T$ for $G = 0.44$ eV, $E = 0.16$ eV. This curve has a first-order transition at $T = 382$ °K, corresponding to Ce at a pressure $p = 11.3$ kbar.

tion-band states, can be included; in this way the infinitely narrow f level becomes, as in Refs. 4–6, a resonant level and the occupation of those states, even at $T = 0$, is never zero. (This would explain why the number of conduction electrons per atom in the α phase is, according to the Hall effect, 3.63 instead of 4.)

(c) Interactions between itinerant quasiparticles should be taken into account.

(d) The effects of the long-range part of the quasiparticle interaction should be studied.

(e) The interaction should be included in higher order of perturbation theory instead of in the mean-field approximation, as is done in this calculation.

III. DISCUSSIONS AND CONCLUSIONS

The model discussed in Sec. II can now be applied to our problem, namely, the α-γ phase transition in Ce metal. If we take the values of J for Ce^{3+} and Ce^{4+} as known, and the density-of-state function is taken to be 20 states/Ry atom and constant, as shown in Fig. 2, the only parameters to be determined, as a function of pressure p, are E and G.

Let us consider first the critical pressure p_C, which we take to be

$$p_C = 19.5 \text{ kbar} \tag{3.1}$$

from experiment (see Fig. 1). At that pressure, we know that the transition is of the critical type shown in Fig. 4. We also know from experiment (Fig. 1), that the critical temperature T_C is around 580 °K, which we take to be

$$T_C = 579 \text{ °K} . \tag{3.2}$$

Critical behavior imposes a one-to-one correspondence between E and G, and (3.2) then determines their values uniquely. In our case, these values are

$$E_C = 0.1894 \text{ eV} , \tag{3.3}$$

$$G_C = 0.44 \text{ eV} . \tag{3.4}$$

These are the values corresponding to the curve of Fig. 4.

As the pressure p is varied from its critical value p_C in the experimental region, most physical parameters (volume and lattice constants in each phase, energy levels, charge densities, and interaction constants) change by a few percent. For instance, as shown in Fig. 1, the lattice parameter in the α phase changes, at room temperature,[2] from 4.85 Å at 10.5 kbar to 4.73 Å at 49.5 kbar, a change of 2.5%. The outstanding exception is the parameter E; E is an energy difference between the energies of an f level and a hybridized s-d conduction band. The energies of each of these with respect to the vacuum level change by a few percent, but the difference energy, i.e., the value of E,

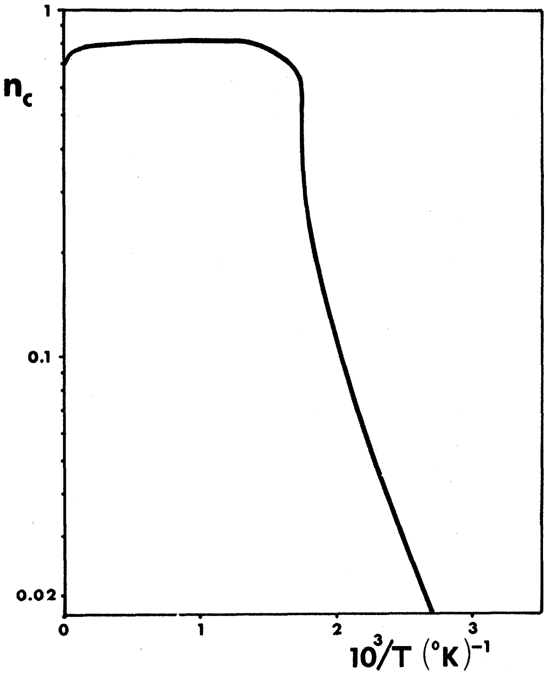

FIG. 4. Plot of n_c as a function of $1000/T$ for $G = 0.44$ eV, $E = 0.1894$ eV. This curve shows critical behavior, corresponding to Ce at a critical pressure $p_C = 19.5$ kbar with a critical temperature $T_C = 579$ °K.

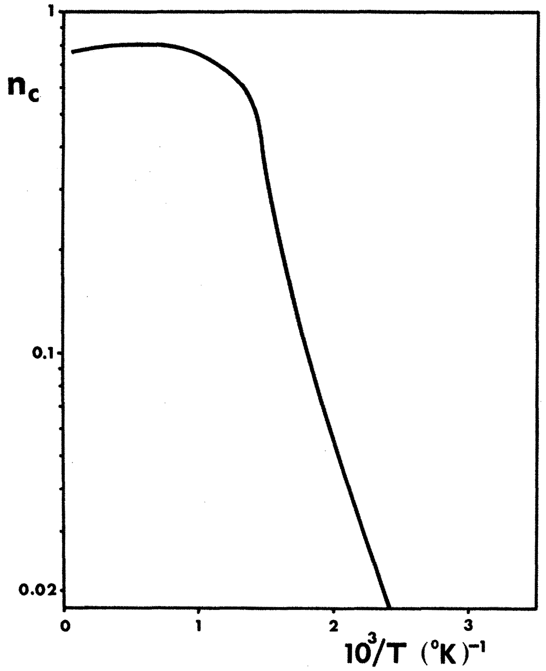

FIG. 5. Plot of n_c as a function of $1000/T$ for $G = 0.44$ eV, $E = 0.21$ eV. This curve corresponds to Ce at a pressure higher than p_C, approximately $p = 25.8$ kbar.

might change by much more, even by an order of magnitude.

It is therefore an excellent first approximation to assume that, as a function of p, the W_e, W_h, and G remain unchanged, while E varies appreciably with p.

If in this fashion E is reduced to 0.16 eV, the graph of Fig. 3 results: There is, in this case, a first-order phase transition at 382 °K, which according to the experimental curve of Fig. 1 corresponds to a pressure $p = 11.3$ kbar.

Therefore by varying E and comparing the transition temperatures T_0 with the experimental values the following approximate relation can be established:

$$E(\mathrm{eV}) = \begin{cases} 0.118 + 0.00375p(\mathrm{kbar}), & p < 16.6\ \mathrm{kbar} \\ 0.126 + 0.00326p(\mathrm{kbar}), & p > 16.6\ \mathrm{kbar}\ . \end{cases} \tag{3.5}$$

If the experimental relationship between transition temperatures T_0 and transition pressures p_0 is used,

$$T_0\ (^\circ\mathrm{K}) = 116 + 23.73p_0\ (\mathrm{kbar})\ , \tag{3.6}$$

the value of T_0 for a known value of E is given by

$$T_0\ (^\circ\mathrm{K}) = \begin{cases} -630 + 6335E\ (\mathrm{eV}), & 0.12 < E \leqq 0.18 \\ -801 + 7286E\ (\mathrm{eV}), & 0.18 < E \leqq 0.1894. \end{cases} \tag{3.7}$$

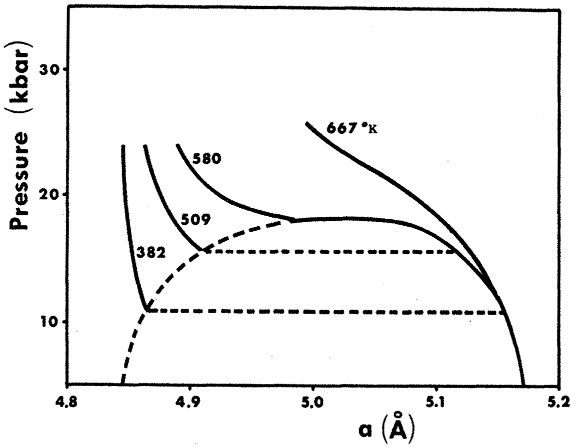

FIG. 6. Isotherms in the pressure-lattice constant diagram. Values of the lattice constant in the γ phase follow the critical curve too closely, so that different isotherms cannot be graphically distinguished from one another and from the critical curve.

Formulas (3.5)–(3.7) are only valid for $E \leqq E_C$, $p \leqq p_C$. We can safely assume, however, that the error in extrapolating (3.5) beyond p_C is not a large one. Therefore a value of $E = 0.21$ eV, which yields the smooth curve for n_c as a function of $1000/T$ shown in Fig. 5, should correspond to an approximate pressure $p \simeq 25.8$ kbar.

The model can yield much more information. For instance, if we know n_c at a given pressure and temperature, the number of conduction n electrons per Ce ion is given by

$$n(p,\ T) = 4 - n_c(p,\ T)\ . \tag{3.8}$$

We may, in addition, assume a linear relationship

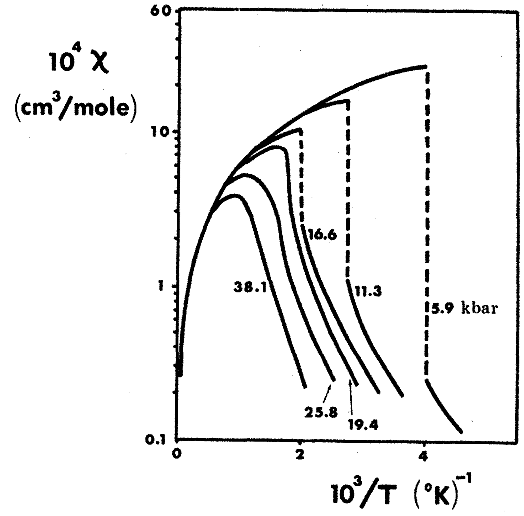

FIG. 7. Paramagnetic susceptibility χ for Ce metal as a function of $1000/T$ for various pressures.

between the lattice constant a_0 and the occupation of the f levels n_c. From room-temperature data ($T_0 = 300\,^\circ\mathrm{K}$, $E = 0.147$ eV) and experimental values[2] we find

$$a_0\ (\text{Å}) = 4.843 + 0.333 n_c\ , \qquad (3.9)$$

which now gives the values of the lattice constant for any pressure and temperature. Isotherms in the p-a_0 diagram are shown in Fig. 6.

We can also calculate the paramagnetic susceptibility of the system. If we neglect the conduction electron contribution, only the Ce^{3+} ions contribute to χ, and at a given pressure and temperature there are only $N n_c(p, T)$ of them, where N is the number of Ce atoms in the crystal. Therefore,[25]

$$\chi = [NgJ(J+1)\,\mu_B^2/3k_B]\,[n_c(p,\ T)/T]\ , \qquad (3.10)$$

where μ_B is the Bohr magneton, $J = \frac{5}{2}$, and $g = 0.811$, values corresponding to Ce^{3+}. A plot of χ as a function of $1000/T$ for various values of p is shown in Fig. 7. We see that in all cases, at high temperatures χ satisfies the Curie law behavior T^{-1}. For pressures $p < p_C$, χ has a discontinuous change at the transition temperature T_0. For $p > p_C$ no such change appears, but χ still exhibits a very anomalous behavior, with an initial increase, a maximum value at a fairly high temperature ($> T_C = 579\,^\circ\mathrm{K}$), and an asymptotic T^{-1} decrease which most of the times cannot be achieved before the melting temperature. As far as we are aware, no experimental values of $\chi(T)$ at high pressures are reported in the literature, and it will be interesting to see, when and if the data became available, whether the predictions of this model are confirmed experimentally.[26]

ACKNOWLEDGMENT

The authors would like to acknowledge a fruitful conversation with Professor M. J. Zuckermann which reactivated their interest in this subject.

---

*Chile-California Cooperative Program Fellow (supported by the Ford Foundation); present address: Departamento de Fisica, Facultad de Ciencias Fisicas y Matematicas, Universidad de Chile, Casilla 5487, Santiago, Chile.

†Work supported in part by the National Science Foundation, through Grant No. GP13889.

[1] E. King, J. A. Lee, I. R. Harris, and T. F. Smith, Phys. Rev. B 1, 1380 (1970).

[2] E. Franceschi and G. L. Olcese, Phys. Rev. Letters 22, 1299 (1969).

[3] D. B. McWhan, Phys. Rev. B 1, 2826 (1970).

[4] A. Blandin, B. Coqblin, and J. Friedel, in *Physics of Solids at High Pressures*, edited by C. T. Tomizuka and R. M. Emrick (Academic, New York, 1965), p. 233.

[5] B. Coqblin and A. Blandin, Advan. Phys. 17, 281 (1968).

[6] C. F. Ratto, B. Coqblin, and E. Galleani D'Agliano, Advan. Phys. 18, 489 (1969).

[7] K. A. Gschneider, Jr., R. O. Elliott, and R. R. McDonald, J. Phys. Chem. Solids 23, 555 (1962).

[8] Y. A. Rocher, Advan. Phys. 11, 233 (1962).

[9] H. Tracy Hall, J. Dean Barnett, and L. Merrill, Science 139, 111 (1963).

[10] K. A. Gschneider, Jr. and R. Smoluchowski, J. Less-Common Metals 5, 374 (1963).

[11] R. I. Beecroft and C. A. Swenson, J. Phys. Chem. Solids 15, 234 (1960).

[12] E. Ponyatovskii, Dokl. Akad. Nauk SSSR 120, 1021 (1958) [Soviet Phys. Doklady 3, 498 (1958)].

[13] A. Jayaraman, Phys. Rev. 137, A179 (1965).

[14] W. H. Zachariasen, Phys. Rev. 76, 301 (1949).

[15] L. Pauling, J. Chem. Phys. 18, 145 (1950).

[16] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1966), p. 437.

[17] See, for instance, S. C. Keeton and T. L. Loucks, Phys. Rev. 168, 672 (1968); O. K. Andersen and T. L. Loucks, *ibid.* 167, 551 (1968).

[18] H. W. Myron and S. H. Liu (private communication).

[19] We are grateful to Dr. T. Loucks for pointing out this to us. It is surprising that most authors neglect to mention in their papers explicitly the fact that the $l = 3$ solutions are usually left out of the calculation.

[20] N. F. Mott, Rev. Mod. Phys. 40, 677 (1968).

[21] L. M. Falicov and J. C. Kimball, Phys. Rev. Letters 22, 997 (1969).

[22] R. Ramirez, L. M. Falicov, and J. C. Kimball, Phys. Rev. B 2, 3383 (1970).

[23] D. L. Johnson and D. K. Finnemore, Phys. Rev. 158, 376 (1967).

[24] Calculations similar to the one presented here have been carried out with more complicated and more realistic density-of-state curves. They involve complicated numerical integrations but add very little to the basic understanding of the phenomena discussed here.

[25] C. Kittel, Ref. 16, p. 436.

[26] *Note added in proof.* Experimental data are now available. See M. R. MacPherson, D. Wohlleben, M. B. Maple, and G. E. Everett, Phys. Rev. Letters 26, 20 (1971).