

The signs reflect the fact that ϵ is intrinsically positive for AuFe-7 and AuFe-1. The best values of ϵ are obtained by generating second differences such that g_0 and hence the error in g_0 vanishes, namely

$$\begin{aligned} Y^{(1)} &= (x_6 - x_2) - (x_6 - x_1), \\ Y^{(2)} &= (x_6 - x_3) - (x_4 - x_1), \\ Y^{(3)} &= (x_6 - x_4) - (x_3 - x_1), \\ Y^{(4)} &= (x_6 - x_5) - (x_2 - x_1). \end{aligned} \quad (\text{A8})$$

All of the above second differences equal 4ϵ . Since these quantities are not independent of each other they must not be combined. Recalling that $\Delta X_{nm}^{(1), (2), (3)} \approx \Delta X'$ ($=0.04$ mm/sec) is independent of line position, one concludes that the best value of ϵ is obtained from any one of the four second differences above. We have arbitrarily chosen $Y^{(4)}$.

Since $\Delta X'$ is independent of line position, the error in a second difference is twice the error in the line position,

$$\Delta Y^{(4)} = 2\Delta X'.$$

The quadrupole shift is

$$\epsilon = \frac{Y^{(4)}}{4};$$

therefore the rms error in ϵ is

$$\Delta\epsilon = \frac{\Delta Y^{(4)}}{4} = \frac{1}{2}\Delta X' = 0.02 \text{ mm/sec.}$$

We make no attempt to extract the quadrupole shift from the class-II spectra.

C. Determination of the Isomer Shift

For class-I spectra, the isomer shift is given by

$$\delta = \frac{1}{6} \left(\sum_{n=1}^6 x_n - 2\epsilon \right). \quad (\text{A9})$$

Substituting for ϵ any of the four second differences of Eq. (A8), one obtains for the rms error in the isomer shift

$$\Delta\delta = (\sqrt{7})/6\Delta X' = 0.02 \text{ mm/sec.}$$

If the quadrupole shift is *a priori* zero, the rms error from Eq. (A9) is

$$\delta = \Delta X'/\sqrt{6}.$$

The isomer shift of the class-II spectra can be estimated from the mid point of the Γ_0^4 measurement. Accordingly we have found no measurable difference in the isomer shift of the class-II compared to the class-I spectra.

High-Temperature Magnetic Susceptibility of Lanthanum and Cerium Metals*

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The magnetic susceptibilities of cerium and lanthanum metals have been measured from room temperature through the melting point. Cerium has a unique fusion behavior with a negative melting slope which has been attributed to a $4f-5d$ electronic promotion. It is demonstrated that this promotion in cerium does not occur and that the small change in the susceptibility at cerium's two high-temperature phase transformations can be attributed almost entirely to changes in the Pauli susceptibility. A quantitative estimate of this change is found by comparison with the lanthanum high-temperature susceptibility.

I. INTRODUCTION

DURING the past few years, careful attention has been paid to the magnetic properties of metallic cerium. The motivation for the present high-temperature susceptibility measurements comes from very recent work on the fusion curve of cerium by Jayaraman¹ in which he suggests that an electronic promotion of the $4f$ electron to the $5d$ conduction band occurs at the melting point for pressures below 30 kbar. The cerium fusion curve is unique in that it has an

initially negative slope followed by a broad minimum. The phase diagram for cerium (Fig. 1) shows that as the pressure is increased below 275°C cerium undergoes an abrupt transformation from a γ phase to an α phase. Both phases possess face-centered-cubic (fcc) structure, but the lattice constant of the α phase is smaller than that of the γ phase. The γ -to- α transition is believed to end in a critical point.^{2,3} If one extrapolates the transition line beyond the critical point, it meets the fusion curve at its minimum. At temperatures above the

* Supported in part by the National Science Foundation and the Office of Naval Research, Nonr 233 (88).

¹ A. Jayaraman, Phys. Rev. **137**, A179 (1965).

² R. I. Beechcraft and C. A. Swenson, J. Phys. Chem. Solids **15**, 234 (1960).

³ B. L. Davis and L. H. Adams, J. Phys. Chem. Solids **25**, 379 (1964).

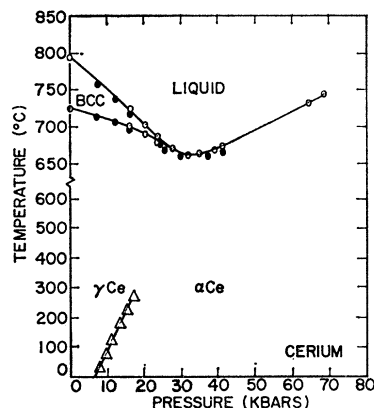


FIG. 1. Phase diagram for cerium metal.

critical point, γ cerium is believed to transform smoothly, though somewhat rapidly to α cerium as the pressure is increased beyond the extrapolated transition line. This transition corresponds to a smooth density variation in the solid.

There is a volume change ΔV associated with the melting transition. The density of the liquid cerium remains nearly constant with pressure, whereas that of the solid changes with pressure. Thus, the volume change ΔV varies with pressure and is related to the slope of the fusion curve by the Clapeyron equation $dT/dp = \Delta V/\Delta S$. The slope is controlled by ΔV since the heat of fusion, hence ΔS , does not appear to be appreciably pressure-dependent. Therefore, the minimum in the fusion curve is thought to be a consequence of the rapid change in density of solid fcc cerium in the region of the fusion curve.

It has been inferred from x-ray and neutron-diffraction investigations⁴⁻⁶ that the change in density associated with the γ -to- α transition in cerium is caused by the electronic transition of the $4f$ electron to the $5d$ conduction band. The neutron-diffraction data, in particular, are in agreement with the hypothesis that the α cerium has no magnetic moment. The decrease in volume associated with the $4f$ - $5d$ electronic promotion has been justified by arguing that when the promotion occurs, the screening of the outer d - and s -like electrons from the nuclear charge is reduced, thereby drawing in these outer electrons.

From the slope of the fusion curve and the heat of transition, the decrease in volume at the melting transition has been calculated by Jayaraman. He finds a value $-0.228 \text{ cm}^3/\text{mole}$, of the same order of magnitude as that obtained by pycnometric density measurements⁷ on liquid cerium. Jayaraman has therefore suggested that the atoms in the liquid phase also have

⁴ A. W. Lawson and T. Y. Tang, *Phys. Rev.* **76**, 301 (1949).

⁵ M. K. Wilkinson, H. R. Child, C. J. McHargue, W. C. Koeller, and E. D. Wollan, *Phys. Rev.* **122**, 1409 (1961).

⁶ C. J. McHargue and H. L. Yakel, Jr., *Acta Met.* **8**, 637 (1960).

⁷ L. J. Wittenberg, D. Ofte, and W. G. Rohr, *Rare Earth Research II*, edited by K. S. Vorres (Gordon and Breach, Science Publishers, Inc., New York, 1964), p. 257.

experienced the $4f$ - $5d$ electronic promotion. If a localized atomic-like state is associated with the $4f$ electron, the magnetic moment presumably would disappear after the $4f$ - $5d$ promotion and the magnetic susceptibility should decrease sharply as the cerium is heated through the melting point. The present investigation was carried out to see if this promotion does occur. The magnetic susceptibility was measured from room temperature through the melting transition. The results indicate that the susceptibility changes only slightly at the melting point and that therefore the proposed $4f$ - $5d$ promotion does not occur.

In addition, we have performed low-temperature measurements to see if the complex low-temperature behavior of the magnetic susceptibility of cerium⁸⁻¹³ might be influenced by sample purity. Using 99.999% pure cerium, we find that Lock's results remain unaltered. An interesting additional result of our low-temperature measurements, which has not been reported previously, is the dependence of the susceptibility on the time elapsed after cooling (Fig. 2). This behavior demonstrates that the low-temperature susceptibility of cerium metal depends not only on the thermal history¹² and rate of cooling,¹⁴ but also on the time elapsed before the measurements are made.

Lanthanum has no $4f$ electron, so its susceptibility is due primarily to the Pauli term. We also carried out high-temperature measurements on lanthanum in order to determine the effect of phase transformations on the Pauli susceptibility. At room temperature, lanthanum has a hexagonal-close-packed (hcp) structure, trans-

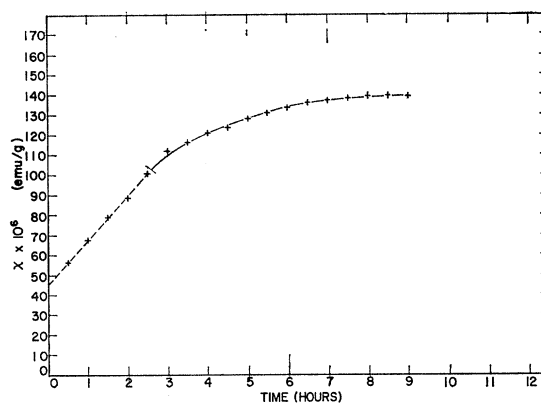


FIG. 2. Magnetic susceptibility of cerium metal at 4.5°K as a function of time after cooling.

⁸ W. Klemm and H. Bommer, *Z. Anorg. Allgem. Chem.* **231**, 138 (1937).

⁹ F. Trombe, *Ann. Phys. (Paris)* **7**, 385 (1937); *Compt. Rend.* **198**, 1591 (1934); **219**, 90 (1944); F. Trombe and M. Foex, *Ann. Chim. (Paris)* **19**, 417 (1944).

¹⁰ C. H. La Blanchetais, *Compt. Rend.* **220**, 392 (1945).

¹¹ H. Leipfinger, *Z. Physik* **150**, 415 (1958).

¹² J. M. Lock, *Proc. Phys. Soc. (London)* **70**, 566 (1957).

¹³ L. M. Roberts and J. M. Lock, *Phil Mag* **2**, 811 (1957).

¹⁴ K. Gschneidner, *Rare Earth Alloys* (D. Van Nostrand, Inc., New York, 1961).

forming at 310°C to an fcc structure, and at 864°C to a body-centered-cubic (bcc) structure. Thus, the high-temperature structural changes are similar to those occurring in cerium, enabling us to correlate the Pauli susceptibility in both metals.

II. EXPERIMENTAL PROCEDURES

The cerium metal, purchased from Research Chemicals, Phoenix, Arizona, was stated to be 99.999% pure with respect to other rare earths. Spectrographic analysis showed that the only detectable impurity was silicon (0.0042%). It is believed that the silicon is an impurity introduced into the surface of the sample by the emery paper used to clean the surface. The lanthanum was obtained from Electronics Space Products Incorporated, Los Angeles, California, and had a stated purity of 99.9%.

To avoid oxidation, the metals were cut with non-ferrous tools under gettered kerosene. While still under kerosene the sample was smoothed and shaped with fine emery paper into the form of a cylinder weighing about 0.2 g. The sample was washed with gettered benzene to remove the less volatile kerosene, wrapped with tantalum foil and dropped into a small quartz tube fitted with a vacuum stopcock. The tube was then evacuated and the sample subsequently sealed in a small section of the quartz tube.

The measurements were made by the Faraday method, using a sensitive Cahn electrobalance and an Alpha Science magnet with pole pieces specially tapered to give a constant BdB/dz . Measurements showed that

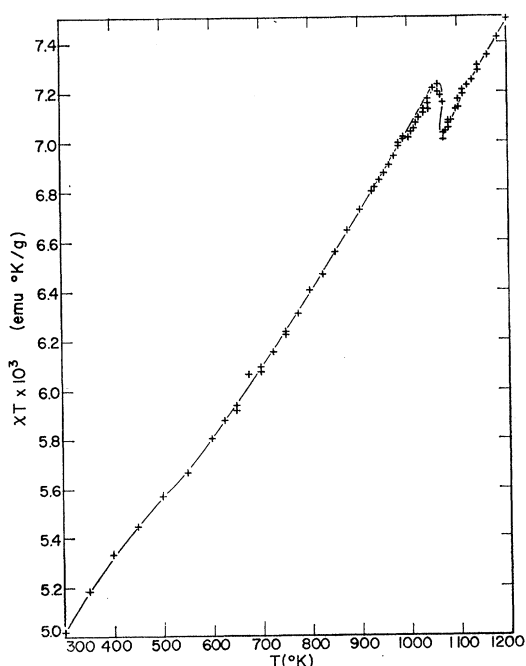


FIG. 3. Magnetic susceptibility of cerium metal as a function of temperature.

this quantity was constant over the dimensions of the sample and its magnitude was determined as accurately as possible by measuring the susceptibilities of crystalline ferric ammonium alum and pure scandium and tantalum metals. The furnace was made of nichrome resistance wire surrounded by a water-cooled copper jacket. Temperatures in the furnace were measured by a (platinum-10%-rhodium)-versus-platinum thermocouple placed just below the sample. The melting point of the cerium, associated with a small decrease in the susceptibility (Fig. 3) occurred at $797 \pm 3^\circ\text{C}$, in good agreement with published values of the melting temperature.¹⁴ An additional check on the temperature readings of the thermocouple was provided by comparison with the susceptibility of Gd_2O_3 from 300–1200°K. Good agreement was obtained.

III. RESULTS

The susceptibility values obtained in this investigation agree qualitatively with those reported earlier.^{15–17} The values obtained at higher temperatures are somewhat smaller than those obtained by the previous investigators. The difference is due in all probability to the considerably higher purity of the cerium used in this investigation. The results are displayed in Fig. 3. There is a slight decrease in the susceptibility at the melting point 1070°K of the order of 3% of the susceptibility at that point. However, the susceptibility does not decrease drastically upon passing through the melting point, indicating that no $4f-5d$ electronic promotion occurs.

The results of the measurement of the susceptibility of metallic lanthanum appear in Fig. 4. Lanthanum is of particular interest because the Pauli part of the

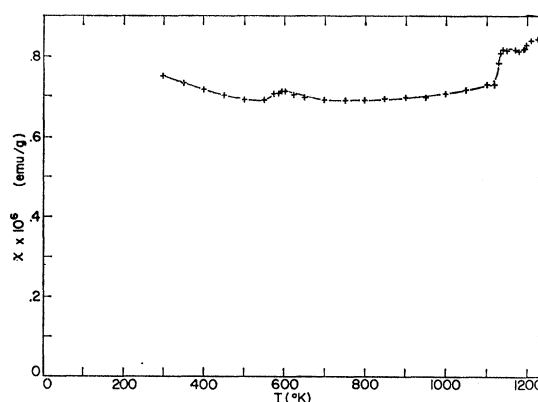


FIG. 4. Magnetic susceptibility of lanthanum metal as a function of temperature.

¹⁵ L. F. Bates, S. J. Leach, and R. G. Loasby, Proc. Phys. Soc. (London) **B68**, 859 (1955).

¹⁶ R. V. Colvin, S. Arajs, and J. M. Peck, Phys. Rev. **122**, 14 (1961).

¹⁷ V. I. Checkernikov and I. Pop, Fiz. Metal. i Metalloved. **18**, 363 (1964). [English transl.: Phys. Metals Metallog. (USSR) **18** (1965).]

cerium susceptibility is expected to be similar at high temperatures. The lanthanum susceptibility shows a slight cusp in the neighborhood of 590°K which can be associated with the onset of the hexagonal-fcc transition. Inspection of Fig. 4 also indicates that there is an increase in the susceptibility of lanthanum at 1135°K and at 1195°K, corresponding to the fcc-bcc and melting transitions, respectively. This does not appear, at first glance, to bear any relation to the case of cerium, where there is a very small change in the susceptibility at the fcc-bcc transition and, in fact, a decrease at the melting transition. However, it will be shown in Sec. IV that they can be correlated.

IV. DISCUSSION

A. Cerium Metal

Previous investigators^{15,16} have apparently been able to explain the high-temperature susceptibility of cerium metal on the basis of a Van Vleck theory,¹⁸ considering thermal excitations from the ground ${}^2F_{5/2}$ level to the ${}^2F_{7/2}$ level. It is, however, also possible approximately to fit the data in Fig. 3 by using a simple Curie-Weiss law, as was shown by Rocher.¹⁹ In fact, one can fit the data in Fig. 3 reasonably well by the formula

$$\chi = (4200/T + 2.74) \times 10^{-6} \text{ emu/g.} \quad (1)$$

Nevertheless, it was decided to try to fit the cerium data by including crystalline field effects, as done by Murao and Matsubara.²⁰ They were able to explain Lock's complex low-temperature susceptibility data by the introduction of a crystalline field and it was felt that the slight decrease in χ at the melting point and the lack of change at the fcc-bcc transition might also be associated with crystalline-field effects.

The Hamiltonian is of the form

$$H = \sum_i \xi(r_i) \mathbf{l}_i \cdot \mathbf{s}_i + V, \quad (2)$$

where the first term represents the spin-orbit coupling and the second the crystalline-field potential. This potential can be expanded in spherical harmonics:

$$V = \sum_{n,m} A_n^m r^n Y_n^m(\theta, \phi). \quad (3)$$

For a cubic crystalline field and a ground ${}^2F_{5/2}$ level, one requires two constants A_4^0 and A_6^0 . The wave functions appropriate to the cubic symmetry must transform according to the representations of the cubic group. In an fcc or bcc lattice of positive ions, the ${}^2F_{5/2}$ level splits into Γ_7 and Γ_8 states, with the Γ_7 lowest; the ${}^2F_{7/2}$ into Γ_6 , Γ_7^+ and Γ_8^+ states. The energy eigenvalues

associated with these states can be found by the method of operator equivalents²¹ to be approximately

$$\begin{aligned} E_{\Gamma_6} &= \frac{3}{2}\zeta + (16/11)A_4^0\langle r^4 \rangle + (1600/429)A_6^0\langle r^6 \rangle \\ E_{\Gamma_8^+} &= \frac{3}{2}\zeta + (16/21)A_4^0\langle r^4 \rangle - (1280/429)A_6^0\langle r^6 \rangle \\ E_{\Gamma_7^+} &= \frac{3}{2}\zeta - (144/77)A_4^0\langle r^4 \rangle + (320/143)A_6^0\langle r^6 \rangle \\ E_{\Gamma_8} &= -2\zeta + (16/77)A_4^0\langle r^4 \rangle \\ E_{\Gamma_7} &= -2\zeta - (32/21)A_4^0\langle r^4 \rangle, \end{aligned} \quad (4)$$

where the superscript plus on the Γ_7 and Γ_8 refers to the excited multiplet. These energies can then be used in the Van Vleck formula for the susceptibility

$$\chi = N \sum_{n,m} [(\mu_{nm}^{(1)})^2/kT - 2\mu_{nm}^{(2)}] e^{-E_n/kT}, \quad (5)$$

where

$$\begin{aligned} \mu_{nm}^{(1)} &= \langle \psi_{nm} | \mu_z | \psi_{nm} \rangle \\ \mu_{nm}^{(2)} &= \sum_{n'} \frac{|\langle \psi_{nm} | \mu_z | \psi_{n'm} \rangle|^2}{E_n - E_{n'}} \\ \mu_z &= \beta(L_z + 2S_z) \end{aligned}$$

to fit to the measured susceptibility. The complexity of Eqs. (4) and (5) forced us to use calculated values²² for $\langle r^4 \rangle$ and $\langle r^6 \rangle$ and to use point-charge approximations for the ratio of A_4^0 to A_6^0 . Once the ratio $A_4^0\langle r^4 \rangle/A_6^0\langle r^6 \rangle$ was calculated, the magnitude of A_4^0 could be found from the crystalline field splitting Δ of the ground multiplet. In this manner the number of parameters could be reduced to two: Δ and ζ , the spin-orbit splitting.

Of course, it cannot be argued that the point-charge model forms a good approximation for a metal. In fact, its straightforward application to cerium results in a crystalline-field splitting $\Delta/k = 600^\circ\text{K}$. This is to be compared with the value 206°K obtained by Murao and Matsubara²⁰ by fitting to specific-heat data. The difference is due, in all probability, to screening by the conduction electrons. Nevertheless, one might hope that at least the sign of the crystal-field parameters, which is just a consequence of the point-group symmetry, is properly given by this crude model.

The introduction of the energies and matrix elements into the Van Vleck formula (5) produces the following result for the fcc phase, if we take the crystalline field and spin-orbit splittings to be $\Delta/k = 206^\circ\text{K}$ (the value obtained by Murao and Matsubara²⁰) and $\zeta/k = 3240^\circ\text{K}$ (the value obtained by Lang²³):

$$\chi = (CF(T))/(T + \theta F(T)) + \chi_p, \quad (6)$$

¹⁸ J. H. Van Velck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932).

¹⁹ Y. A. Rocher, *Advan. Phys.* **11**, 233 (1962).

²⁰ T. Murao and T. Matsubara, *Progr. Theoret. Phys. (Kyoto)* **18**, 215 (1957).

²¹ R. J. Elliott and K. W. H. Stephens, *Proc. Roy. Soc. (London)* **A218**, 553 (1952); **A219**, 387 (1952); K. W. H. Stephens, *Proc. Phys. Soc. (London)* **A65**, 209 (1952).

²² A. J. Freeman and R. E. Watson, in *Magnesium*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. II A.

²³ R. J. Lang, *Can. J. Research* **14**, 127 (1936).

where

$$F(T) = (2(1 + 2e^{(206/T)} + e^{(-3282)/T} + 2e^{(-3395)/T} + e^{(-3735)/T}))^{-1} \\ \times ((1.0204 + 0.031932) + (5.3061 - 0.031368T)e^{(-206)/T} + (5.8776 + 0.14222T)e^{(-3282)/T} \\ + (9.4331 - 0.08116T)e^{(-3395)/T} + (3.5556 - 0.06176T)e^{(-3735)/T}).$$

Here, χ_p is the temperature-independent Pauli susceptibility. The Curie-Weiss constant θ has been introduced to account for exchange interactions in the molecular field approximation, following Murao and Matsubara.²⁰ If the influence of the excited levels arising from the $^2F_{7/2}$ level is eliminated in (6), our result reduces to the expression obtained by them. The data appearing in Fig. 3 can be fit by Eq. 6 if one takes χ_p to be 1.4×10^{-6} emu/g and $\theta = 9^\circ\text{K}$. One might expect the Pauli susceptibility for cerium to be about equal to that for lanthanum (0.75×10^{-6} emu/g) from a density of states argument. The low-temperature specific heats of lanthanum and cerium are not greatly different if one subtracts from cerium the magnetic contribution due to antiferromagnetic ordering. The fit to the data by Eq. (6) is not very sensitive to changes in χ_p , so the difference between the value extracted for cerium, $\chi_p = 1.4 \times 10^{-6}$ emu/g, and the Pauli susceptibility of lanthanum may not be significant.

B. Lanthanum Metal

Jayaraman²⁴ calculates from the phase diagram an increase in volume of $+0.14$ cm³/mole for lanthanum metal at both the fcc-bcc transition and the melting point. However, from a consideration of published values^{14,25} of the density and thermal expansion of lanthanum, the fcc-bcc transition would be expected to have an associated volume change of about $+0.35$ cm³/mole. The volume change $+0.14$ cm³/mole at the melting point is not in disagreement with other data. We could use these changes in atomic volume to calculate a change in density of states in the free-electron approximation and from this change the change in Pauli susceptibility could be estimated. For volume changes of $+0.35$ and $+0.14$ cm³/mole at the fcc-bcc and melting transitions, we would estimate a free-electron change in susceptibility of $+0.008$ and $+0.003 \times 10^{-6}$ emu/g, respectively. These are to be compared with experimental values (Fig. 4) of ± 0.08 and $+0.025 \times 10^{-6}$ emu/g. It is seen that a free-electron model yields changes in χ_p of the same sign and in approximately the same ratio as that found experimentally, but that the predicted values are smaller than the measured values by a factor of 10.

C. Correlation of Results

From the phase diagram for cerium, Jayaraman calculates volume changes of -0.037 and -0.228 cm³/mole at the fcc-bcc and melting transitions, and these are not in disagreement with published values^{7,14,25}

of density and thermal expansion. Using these values, one calculates changes in Pauli susceptibility at the fcc-bcc and melting transition of -0.001 and -0.007×10^{-6} emu/g. If we assume that, as in lanthanum, these free-electron values are too small by a factor of 10, then the values predicted for cerium metal are -0.01 and -0.07×10^{-6} emu/g, respectively. There are also changes in the f -electron paramagnetism due to structural changes. The change in crystal field constants A_4^0 and A_6^0 due to the different symmetry, can be estimated from a modified point-charge approximation using the same assumptions as in A. The crystalline-field coefficients were calculated, including the contributions from first-, second- and third-nearest neighbors. The change in the crystalline field at the melting point was estimated by dropping the contribution from second- and third-nearest neighbors. The contribution from the first-nearest neighbors is retained because of the well known short-range order in the liquid state. The changes in f -electron paramagnetism at the fcc-bcc and melting transitions are found to be $+0.03$ and -0.07×10^{-6} emu/g, respectively. Combining these contributions with the changes in Pauli susceptibility, one finds net changes of approximately $+0.02$ and -0.14×10^{-6} emu/g, respectively, to be compared with experimental values of zero and -0.20×10^{-6} emu/g. These results agree in sign and order of magnitude with the calculated changes and give about the best agreement one could expect. Thus it seems that the change in susceptibility in cerium at the melting point can be attributed essentially to the effect of structural changes on the f -electron paramagnetism and Pauli paramagnetism, with apparently no need for a $4f-5d$ promotion.

V. CONCLUSIONS

The measurement of the susceptibility of cerium metal through the melting point has demonstrated that no electronic $4f-5d$ promotion need be assumed. The behavior of the susceptibility at the fcc-bcc and melting transitions can be understood qualitatively on the basis of the effect of the structural changes on the f -electron paramagnetism and Pauli paramagnetism.

Still unanswered, however, is the very puzzling question of why cerium exhibits such an anomalous negative slope and minimum in its fusion curve, whereas lanthanum metal appears to be quite well behaved in the same region.

ACKNOWLEDGMENTS

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²⁴ A. Jayaraman, Phys. Rev. **139**, A691 (1965).

²⁵ *The Rare Earths*, edited by F. H. Spedding and A. H. Daane (John Wiley & Sons, Inc., New York, 1961).