

tions in the **T** and **S** matrices. These additional parameters will not, however, be introduced here as the other authors have not included them.

### (1) The Model of Hardy *et al.*

The equations of motion used by Hardy seem at first sight to be considerably different from Eqs. (1) and (2), which were used in this work. These equations may, however, be written in a similar form to those of Hardy if the effective electric field **E** is introduced. The equations of motion (1) and (2) then become

$$m\omega^2\mathbf{U}=\mathbf{R}\mathbf{U}+\mathbf{T}\mathbf{W}-\mathbf{Z}\mathbf{E}, \quad (\text{A1})$$

$$\text{where } 0=\mathbf{T}^T\mathbf{U}+\mathbf{S}\mathbf{W}-\mathbf{Y}\mathbf{E}, \quad (\text{A2})$$

$$\mathbf{E}=-\mathbf{C}(\mathbf{Z}\mathbf{U}+\mathbf{Y}\mathbf{W}). \quad (\text{A3})$$

When **W** is eliminated from Eqs. (A1) and (A3) and

then **E** is eliminated, a single equation of motion remains;

$$m\omega^2\mathbf{U}=[\mathbf{R}-\mathbf{TS}^{-1}\mathbf{T}^T+(\mathbf{Z}-\mathbf{TS}^{-1}\mathbf{Y})\mathbf{C}(\mathbf{Z}-\mathbf{YS}^{-1}\mathbf{T}^T) \\ -(\mathbf{Z}-\mathbf{TS}^{-1}\mathbf{Y})\mathbf{CYS}^{-1}\mathbf{Y}(\mathbf{I}+\mathbf{CYS}^{-1}\mathbf{Y})^{-1}\mathbf{C}(\mathbf{Z}-\mathbf{YS}^{-1}\mathbf{T}^T)]\mathbf{U},$$

where **I** is the unit matrix. The equation is now of the same form as Eq. (15) of Hardy (1962),<sup>5</sup> apart from Hardy's neglect of the term  $\mathbf{TS}^{-1}\mathbf{T}^T$ , which was mentioned in Sec. III.1.

### (2) The Model of Toyopygo *et al.*

When Eqs. (1) and (2) are compared with Eqs. (1) of Ref. 23, the equations of motion used by Tolpygo *et al.* are easily seen to be similar to those used in this paper. The only difference between the theories is the neglect of short-range dipole-dipole interactions in the **S** matrix, as described above (Sec. III.1).

## Observation of a Possible Large Crystalline Stark Splitting in Metallic Ce:LaAl<sub>2</sub><sup>†</sup>

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The susceptibility of polycrystalline Ce<sub>x</sub>La<sub>1-x</sub>Al<sub>2</sub> with several different concentrations of cerium has been found to decrease to about one fourth the value for free-Ce<sup>3+</sup> ions between room temperature and 4.2°K. The observed behavior is consistent with a cubic-crystal field splitting in the  $J=\frac{5}{2}$  ground term of Ce<sup>3+</sup> of 200°K. The observed splitting is close to that predicted on a point-charge ionic model ignoring shielding by conduction electrons if the rare-earth ions are assumed to be tripositive and the aluminums negative, and if the 4*f* electron of Ce<sup>3+</sup> is represented by a Hartree-Fock function. It is about one third as large as might have been expected on the basis of experience with cubic nonconductors had the Ce:LaAl<sub>2</sub> been a nonconductor with this distribution of charges rather than a conductor.

### INTRODUCTION

ALTHOUGH a considerable body of knowledge has accumulated on the crystalline Stark splittings of energy levels of rare-earth ions in nonconducting, ionic crystals, relatively little is known about the splittings in metallic environments. A broad anomaly in the specific heat of praseodymium metal centered about 50°K provided possibly the first clear evidence that Stark splittings might be appreciable in the rare-earth metals.<sup>1</sup> The anomaly could be fitted by assuming that it arises from a cubic Stark splitting of 80°K between a singlet

and a triplet in the ground term of Pr<sup>3+</sup> ions.<sup>1,2</sup> More detailed calculations based on the actual symmetry of this metal, which is hexagonal rather than cubic, are in progress,<sup>3</sup> and will hopefully also explain the susceptibility,<sup>4</sup> which in simplest approximation requires a considerably smaller Stark splitting.<sup>2</sup>

A maximum in the specific heat of metallic cerium at 100°K has been attributed by Murao and Matsubara<sup>5</sup> to a cubic Stark splitting in the ground term of Ce<sup>3+</sup> of 200–250°K. A splitting of this size is also compatible with the susceptibility of the metal, which, especially on first cooling and warming shows departures from

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<sup>1</sup> D. H. Parkinson, F. E. Simon, and F. H. Spedding, Proc. Roy. Soc. (London) **207**, 137 (1951).

<sup>2</sup> B. Bleaney, J. Appl. Phys. **34**, 1024 (1963).

<sup>3</sup> B. I. Bleaney (private communication).

<sup>4</sup> J. M. Lock, Proc. Phys. Soc. (London) **B70**, 566 (1957).

<sup>5</sup> T. Murao and T. Matsubara, Progr. Theoret. Phys. (Kyoto) **18**, 215 (1957).

Curie-Weiss behavior.<sup>4-6</sup> Although recent neutron scattering experiments have shown that the cubic phase of cerium at low temperatures is magnetically inactive and that the magnetization and specific heat there come entirely from atoms in the hexagonal phase, the value derived for the moment in this phase from the coherent scattering at low temperatures is consistent with a Stark field which is at least predominantly cubic.<sup>7</sup> The other large anomaly in the specific heat of cerium, that at 12.5°K, was found to be too narrow, and to enclose too little entropy, to be a Schottky anomaly corresponding to a small Stark splitting.<sup>1</sup> This anomaly was later shown to be associated with a transition to antiferromagnetism at this temperature.<sup>4,7</sup>

Many other anomalies have been found in the specific heats and magnetic susceptibilities of the rare-earth metals.<sup>8</sup> Many of these are associated with transitions to magnetic order and hence, shed little light on the magnitude of the Stark splittings. In the heavy rare-earth metals these transitions occur at sufficiently high temperatures and are associated with such large energies of ordering that effects of crystalline Stark fields are largely hidden from view. A good example of this is the fact that the anomalies in specific heat attributable to hyperfine structure can be understood in these metals without mentioning Stark splittings.<sup>2</sup> A Stark effect does appear, however, in the measurement of the Mössbauer resonance in thulium metal between 80 and 300°K: The observed dependence of the quadrupole interaction on temperature suggests that the local Stark field at the  $\text{Tm}^{3+}$  ion in this metal is comparable to that in nonconducting  $\text{Tm}_2\text{O}_3$ .<sup>9</sup>

Additional indirect evidence that local Stark fields may be appreciable in the heavy rare-earth metals comes from the fact that the peculiar spin configurations in the magnetically ordered states at low temperatures can be understood if the Stark splittings in the constituent ions are large enough to cause appreciable magnetocrystalline anisotropy.<sup>10,11</sup>

<sup>6</sup> Both the specific heat and magnetic susceptibility of metallic cerium are complicated by a phase transition which occurs in the region 50–200°K. This transition is especially pronounced on first cooling and warming, and has associated with it many striking effects of thermal hysteresis. The transition gradually disappears on repeated thermal cycling. Murao and Matsubara were able to explain the specific heat and susceptibility at low temperatures by assuming that on first cooling about half of the cerium atoms lose their magnetic 4f electrons to a conduction band where they are paired off, and, hence, no longer contribute appreciably to the magnetization, and that fewer and fewer electrons make this transition on subsequent coolings. They were able on this basis to fit the specific heat and the susceptibility both on first cooling and after repeated cycling by assuming cubic Stark splittings in the ground term of  $\text{Ce}^{3+}$  of, respectively, 240 and 206°K.

<sup>7</sup> M. K. Wilkinson, H. R. Child, C. J. Hargue, W. C. Koehler, and E. O. Wollan, *Phys. Rev.* **122**, 1409 (1961).

<sup>8</sup> For recent reviews and discussions of specific heat and related measurements in rare-earth metals, see D. H. Parkinson, *Rept. Progr. Phys.* **21**, 226 (1958), and B. Bleaney, *Refs. 2 and 3*.

<sup>9</sup> R. Mössbauer (private communication).

<sup>10</sup> R. J. Elliott, *Phys. Rev.* **124**, 346 (1961).

<sup>11</sup> Many experiments on rare-earth ions in metals besides those discussed here show effects which may indicate appreciable Stark

We wish in the following sections to present experimental evidence for a large local Stark field at the rare-earth site in another class of metals, the rare-earth aluminides. These intermetallic compounds, with the generic composition  $\text{REAl}_2$ , can be prepared with any rare-earth as a constituent. The rare-earth ion (RE) always appears at a site with cubic symmetry.<sup>12</sup> We have measured the magnetic susceptibility of  $\text{LaAl}_2$  with different fractions of the magnetically inert lanthanum ions replaced by cerium. We have found that below 100°K the susceptibility drops markedly below that to be expected for free- $\text{Ce}^{3+}$  ions, and have been able to interpret the results quantitatively by assuming a cubic Stark splitting of 200°K in the ground term of the  $\text{Ce}^{3+}$  ion. The corresponding local Stark field is nearly the same size and has the same sign as found by Murao and Matsubara for cerium metal. Its origin is different, however, as the immediate environments in the two metals are quite dissimilar, the nearest neighbors in the aluminide, for example, apparently being negatively charged rather than positively charged as in the cerium metal.

## EXPERIMENTAL RESULTS

The susceptibility of polycrystalline samples of  $\text{Ce}_x\text{La}_{1-x}\text{Al}_2$  with concentrations of cerium of  $x=0.012$ , 0.028, 0.039, and 1.0 was measured between 1.4 and 300°K at a field of 14 240 Oe using the pendulum magnetometer of Bozorth, Williams, and Walsh.<sup>13</sup> The susceptibility observed per  $\text{Ce}^{3+}$  ion after subtracting the relatively small and temperature-insensitive susceptibility of undoped  $\text{LaAl}_2$  is shown in Fig. 1. The susceptibility is seen at low temperatures to fall well below that for free  $\text{Ce}^{3+}$  ions, given by the dashed line in the figure. This occurs independently of the concentration of cerium.

In Fig. 2 the magnetization of a sample of pure  $\text{CeAl}_2$  is shown for fields of up to 80 kOe at a temperature of 4.2°K. As is consistent with the small value for the magnetic moment at low temperatures, there is seen to be relatively little saturation even at the highest fields used.

## DISCUSSION

Each rare-earth ion in  $\text{REAl}_2$  is surrounded by 12 aluminum atoms at a distance  $R_{\text{Al}}=3.35$  Å and by four rare-earth atoms almost as close at  $R_{\text{RE}}=3.5$  Å.<sup>12</sup> The potential energy of a cerium electron at  $x, y, z$  resulting from point charges  $Ze$  at each of the neighboring alu-

splittings. To the best of our knowledge, however, it has not yet been possible to pursue the analysis of any of these measurements far enough to determine the magnitude of the local Stark field. The interested reader is referred to the review by B. Bleaney (*Ref. 8*), for a discussion and references to some of these measurements.

<sup>12</sup> J. H. Wernick and S. Geller, *Trans. AIME* **218**, 866 (1960).

<sup>13</sup> R. M. Bozorth, H. J. Williams, and D. E. Walsh, *Phys. Rev.* **103**, 572 (1956).

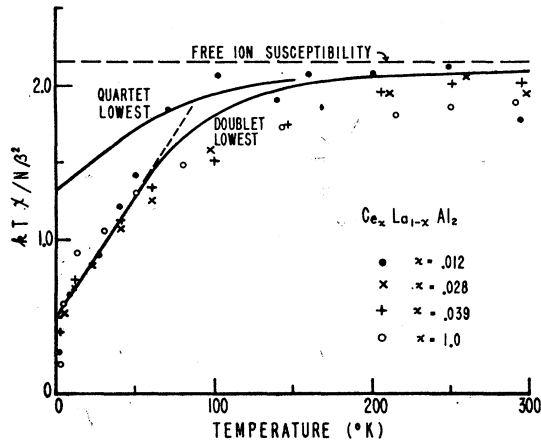


FIG. 1. Susceptibility of Ce:LaAl<sub>2</sub>. The dashed line gives the value for free Ce<sup>3+</sup> ions:  $\chi = N\beta^2\mu_{\text{eff}}^2/kT$  with  $\mu_{\text{eff}}^2 = gJ^2J(J+1)/3 = 2.14$ . The solid curves show the effect of a cubic crystal field splitting of 200°K with either the doublet or quartet levels lowest.

minum atoms is<sup>14,15</sup>

$$V_{\text{Al}} = -\frac{Z_{\text{Al}}e^2}{R_{\text{Al}}} \left[ 12 + \frac{455}{121R_{\text{Al}}^4} \left( x^4 + y^4 + z^4 - \frac{3r^4}{5} \right) \right], \quad (1)$$

while that resulting from the nearest rare-earth neighbors is

$$V_{\text{RE}} = -\frac{Z_{\text{RE}}e^2}{R_{\text{RE}}} \left[ 4 - \frac{35}{9R_{\text{RE}}^4} \left( x^4 + y^4 + z^4 - \frac{3r^4}{5} \right) \right]. \quad (2)$$

[Although sixth- and higher-order terms are also present in the potential, these do not contribute to the splitting within the  $J = \frac{5}{2}$  ground term of the cerium ions and hence have not been displayed in (1) and (2).] Because of the near equivalence of the distances to the nearest aluminum and rare-earth neighbors, the fourth-order fields produced by each are nearly equal in magnitude, though of opposite sign: a positive charge at each aluminum position would produce a negative fourth-order energy, while a positive charge at the rare-earth neighbors (or negative charge at the aluminums) results in a positive energy.

The cubic-crystal field decomposes the ground term

<sup>14</sup> Relative to an origin at a rare-earth atom the  $X, Y, Z$  projections of the nearest aluminum atoms are 1, 1, 3 in units of 1.01 Å, plus the eleven additional sets of projections obtained by cyclic permutation of these three numbers and negation of any two. The positions of the nearest rare-earth neighbors in the same units are  $-2, -2, -2; -2, 2, 2$  plus cyclic permutations. (Although the individual rare-earth sites lack the macroscopic inversion symmetry of the crystal and, hence, are not all equivalent, the fields at these sites are none the less equivalent since the potential depends only on even powers of the projections of the positions of the neighboring ions.)

<sup>15</sup> One of the authors (J.W.) wishes to acknowledge his debt to Professor B. Bleaney for calling his attention to an error in the coefficient of the fourth-order potential used in an early version of this paper; in a brief report of this work which appeared in Bull. Am. Phys. Soc. 8, 65 (1963), the words "negatively charged" should be changed to read "positively charged."

of Ce<sup>3+</sup> into a doublet and a quartet, with the quartet lowest if the potential energy is negative and the doublet lowest if it is positive. A splitting  $h\nu_c$  between these levels reduces the susceptibility from the value for free Ce<sup>3+</sup> ions by the factor

$$f(x) = \frac{(5/21) + (26/21)e^{-x} + (32/21x)(1 - e^{-x})}{1 + 2e^{-x}}, \quad (3)$$

with  $x = h\nu_c/kT$ . This factor is the same as for the  $J = \frac{5}{2}$  term of Sm<sup>3+</sup> in a cubic field, and has been derived for that term by Amelia Frank.<sup>5,16</sup> The sign of the splitting  $h\nu_c$  is to be taken to agree with that of the net fourth-order potential energy.

It is seen from (3) that the susceptibility at  $T = 0$  is reduced by 5/21 if the doublet lies lowest and by 13/21 if the quartet is lowest. The experimental data shown in Fig. 1 clearly converge much more nearly to 5/21 than to 13/21, the value for free ions. Thus, the doublet must lie lowest. This is appropriate for positively charged rare-earth neighbors or/and negatively charged aluminums.

From (3) it is seen that the dependence of the reduction in susceptibility on temperature is given at low temperatures by  $(df/dT)_{T=0} = 32k/21h\nu_c$  when the doublet lies lowest. A straight line drawn through the data for low temperatures gives 1/130°K for this slope, corresponding to a Stark splitting in the ground term of cerium of  $h\nu_c = 200^\circ\text{K}$ . (In determining this slope we have ignored the rapid drop in  $\chi T$  between 4.2 and 1.4°K which may be a result of magnetic ordering at these very low temperatures.) The dependence of the susceptibility on temperature predicted by (3) for a crystal-field splitting of 200°K is shown by a solid curve in Fig. 1. A curve showing the susceptibility for a crystal-field splitting of the same magnitude but opposite sign (i.e.,

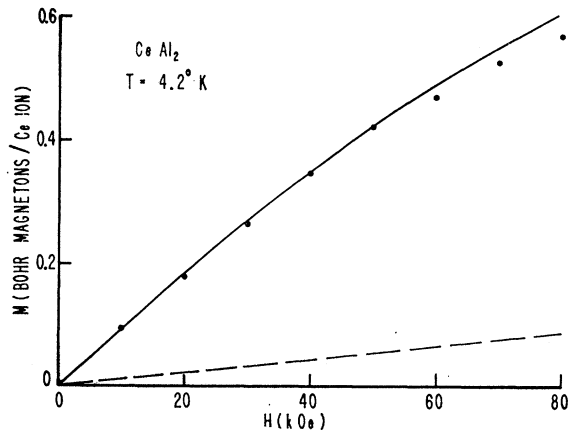


FIG. 2. Dependence of the magnetization of CeAl<sub>2</sub> on magnetic field at 4.2°K. The solid curve gives the theoretical magnetization for a doublet including the contribution (dashed line) from the quartet when the latter is assumed to lie 200°K above the doublet.

<sup>16</sup> A. Frank, Phys. Rev. 48, 765 (1935); J. A. White and J. H. Van Vleck, Phys. Rev. Letters 6, 412 (1961).

with the quartet lowest) is given for comparison in the same figure.

The data displayed in Fig. 1 are seen to be in reasonably good agreement at all but the very lowest temperatures with the theoretical curve which gives the susceptibility for a splitting of 200°K with the doublet lowest. For each concentration of cerium the susceptibility is seen to drop away from that for free ions at about the temperature which is predicted for a splitting of this magnitude. For temperatures above 50°K, however, the experimental points lie typically 5–10% below the theoretical curve. Although there is considerable scatter in the data, this effect seems to be a genuine, though puzzling, one. The concentrations of cerium in the dilute samples as determined by spectroscopic analysis could be in error by as much as 10% but this could not explain the decreased susceptibility for pure CeAl<sub>2</sub>. On the other hand, any residuum of cooperative behavior which might still be in evidence for the pure CeAl<sub>2</sub> at high temperatures should be much less noticeable in the dilute samples. One possible source of the discrepancy might be a lattice contribution to the susceptibility of the individual ions. To the best of our knowledge, the magnitude of this contribution is not yet known for rare-earth ions.<sup>17</sup> The decrease in the susceptibility at high temperatures definitely cannot be due to admixture of the excited  $J = \frac{7}{2}$  term of cerium. In the first place, this should give a paramagnetic rather than diamagnetic contribution for feeble crystal fields. Furthermore, any contribution from this source must be extremely small.<sup>18</sup> Thus, we are unable at present to account for this discrepancy between theory and experiment, but believe it is sufficiently small not to invalidate our conclusion that the data show a large effect due to the crystal Stark field.

For a saturating magnetic field at low temperatures where only the doublet is occupied the magnetization should, except for a small temperature-independent contribution from admixture by the magnetic field of quartet states into this doublet, be one third that for a free ion. The saturation should occur somewhat more rapidly with increasing field than if the ground term of the ion were unsplit.<sup>19</sup>

Figure 2 shows the saturation which was observed

for a sample of pure CeAl<sub>2</sub> subjected to fields of up to 80 kOe at 4.2°K. The data are seen to be in reasonably good agreement with the theoretical curve, which is the sum of the linear, temperature-independent contribution from the quartet lying 200°K above the doublet, given by the dashed line, and the saturating, hyperbolic tangent contribution, from the doublet states. Except at the highest fields where there is seen to be slightly more saturation than predicted, the observed magnetization is in excellent agreement with that predicted.

The observations which have been discussed above all point to a rather large crystalline Stark splitting of 200°K in the ground term of the Ce<sup>3+</sup> ion in the aluminide host. It is interesting to compare this splitting with that which might have been expected for this metal if it had been a nonconductor. If for the fourth power of the radius of the 4f electron we use the Hartree-Fock value of Freeman and Watson,<sup>20</sup> viz.,  $\langle r^4 \rangle_{Ce} = 3.5$  a.u., and assume each rare-earth ion is triply charged positive with the compensating negative charge divided equally among the aluminum atoms, we find a splitting of 180°K due to the nearest rare-earth and aluminum neighbors provided the charges are assumed to be concentrated at points at the atoms. This prediction is very close to the splitting which has been observed. Experiments on nonconductors give splittings which are typically three or four times as large as predicted on the same basis (cf., the discussions for Tm<sup>2+</sup> in CaF<sub>2</sub><sup>21</sup> and for garnets in cubic approximation<sup>22</sup>).

Unfortunately, there are as yet no band calculations for the intermetallic compounds from which to infer the degree to which electrons actually do concentrate at the aluminum sites in these metals at the expense of the rare-earth atoms, or on which to base estimates of the shielding by the conduction electrons. Our observations can be interpreted as evidence that the polarization is smaller, or the shielding larger, by about a factor of 3 than might have been anticipated from experience with ionic nonconductors had the aluminide been a nonconductor with three units of positive charge at each rare-earth atom and a compensating negative charge shared among the aluminum neighbors.

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<sup>17</sup> This effect is currently being studied theoretically by M. Inoue.

<sup>18</sup> Both fourth- and sixth-order terms in the Stark field are operative in the  $J = \frac{7}{2}$  term, and both connect  $J = \frac{7}{2}$  with  $J = \frac{5}{2}$  states. Their effect on the susceptibility is small, however, as can be seen by adapting Miss Frank's discussion of the fourth-order field (Ref. 16) to cerium and from the fact that the sixth-order field normally has somewhat less effect on rare-earth ions in a cubic site, than the fourth-order field: See J. A. White, J. Phys. Chem. Solids **23**, 1787 (1962).

<sup>19</sup> See J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932), Sec. 61.

<sup>20</sup> A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962).

<sup>21</sup> Z. Kiss, Phys. Rev. **127**, 718 (1962); B. Bleaney (to be published).

<sup>22</sup> J. A. White, Ref. 18.