Gyromagnetic Ratios of Metallic Samarium Compounds*

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In metallic rare-earth compounds the exchange interaction between the $4f$ shell and the conduction electrons causes a portion of the conduction-electron magnetization to be added to the magnetization of each rare-earth atom. Because these two magnetization components will, in general, have different gyromagnetic ratios, it follows that the gyromagnetic ratio of the whole material will differ from that of the rare-earth ions alone, which is given by the Landé factor. For the rare-earth metals apart from samarium, the resulting gyromagnetic ratio shifts are estimated to be of the order of 1%, too small to be detected by present experimental methods. However, an exploratory calculation suggests that the shift might be very large, perhaps of the order of 100%, in a samarium compound in which the interactions were of a strength comparable to those which are found in elemental samarium metal.

I. INTRODUCTION

The gyromagnetic ratio[1-4] g' of a body is equal to $-2mc/e$ multiplied by the ratio of its magnetic moment to its angular momentum. It is given by

$$g' = \sum_i \langle l_i^z + 2s_i^z \rangle_T \Big/ \sum_i \langle l_i^z + s_i^z \rangle_T , \tag{1.1}$$

where $\vec{l}_i$ and $\vec{s}_i$ are the orbital and spin angular momentum operators of an electron, the summation is over all electrons in the body, the subscript T denotes a thermal average, and $m, e,$ and c are the mass and the magnitude of the electronic charge, and the velocity of light, respectively. The terms associated with Larmor diamagnetism should be included in the magnetic moment but omitted from the angular momentum.[5] We primarily consider here materials in the paramagnetic state situated in a static magnetic field H in the z direction, and we neglect effects due to nuclear spin.

Many of the magnetic properties of metallic rare-earth materials may be understood as arising from the existence of an exchange interaction $-2\mathcal{J}_{sf}\vec{S}\cdot\vec{s}$ between the spin $\vec{S}$ of the $4f$ shell of a rare-earth and the spin $\vec{s}$ of a conduction electron. In particular, this interaction changes the size of the magnetic moment of a rare-earth ion by adding a portion of the conduction-electron magnetization to it. Since the gyromagnetic ratio of this additional magnetization is equal to 2, and the gyromagnetic ratio of the rare-earth $4f$ shell, which is given by the Landé g factor, is not equal to 2 except for a half-filled shell, it follows that the gyromagnetic ratio g' of the whole material will be different to that of the rare-earth ions alone. The purpose of this paper is to calculate this shift in gyromagnetic ratio for metallic compounds which contain normal rare earths which have wide multiplet splittings, and for those which contain triva-

lent samarium, which has a $J = \frac{7}{2}$ multiplet level only 1550 °K above its $J = \frac{5}{2}$ ground state,[2,6] and which, therefore, needs special consideration.

The effect of conduction-electron polarization upon the susceptibility[7-9] and ordered moment[10] of metallic rare-earth materials has been investigated previously (henceforth, Ref. 7 will be referred to as I). It was predicted that the effects would be very much greater in samarium than in other rare-earth metals for two reasons. The first is that the size of these effects is proportional to the quantity $(g-1)/g$, which is five times larger for samarium's $4f^{5\,6}H_{5/2}$ ground state than for that of any other rare-earth ion. The second is that the paramagnetic moment $g[J(J+1)]^{1/2}\mu_B$ of samarium's ground state ($0.845\mu_B$) is very small to begin with, so that the relative effect of the conduction-electron polarization appears disproportionately large. It was argued in I that, although the magnetic susceptibility of elemental samarium metal seems, at first sight, to be highly anomalous (for example, the effective Curie constant of the double-hexagonal-close-packed phase is more than five times smaller than the free-ion value), the behavior can be explained in terms of exactly the same interactions as are familiar in the heavy rare earths. Samarium behaves as a straightforward rare-earth metal; its apparently strange features have their origins in the unusual multiplet structure of the free ion.

These ideas have received support from the neutron diffraction experiments which Koehler and Moon[11,12] have made on antiferromagnetically ordered rhombohedral samarium. By analyzing the magnetic form factor of the cubic sites using a point-charge crystal-field model they concluded that the ratio of the conduction-electron magnetization per ion to the spin part of the magnetization of the $4f$ shell was $+0.15$. A value of $+0.10$ had been

predicted in I from an analysis of the paramagnetic susceptibility of double-hexagonal-close-packed samarium using a theory which neglected crystal-field effects entirely. Koehler and Moon also confirmed that rhombohedral samarium has a magnetic transition at 106 °K, therefore showing that the analysis which had been given in I of this material was invalid. The possibility that this might be so had been anticipated in the original paper. A further discussion of the interpretation of the susceptibility data for rhombohedral samarium is given in Appendix A of the present paper.

Calculations of the gyromagnetic ratios of tripositive samarium and europium have been made by Frank[1] and Van Vleck,[2] and these have been extended to higher temperatures by Arajs and Colvin[13,14]; neither of these calculations took account of interactions. No experimental work seems to have been done on the gyromagnetic properties of the rare-earth metals.

In Sec. II of this paper we calculate the gyromagnetic ratios of compounds which contain normal rare earths, and in Sec. III the ratios of compounds which contain samarium. Some of the equations have been derived previously in I, and by adopting these directly with the omission of the details of their derivations we are able to shorten the length of this paper. Paper I therefore serves as an introduction to this present one.

II. GYROMAGNETIC RATIOS OF COMPOUNDS CONTAINING NORMAL RARE EARTHS

The starting point for the calculation is the static[15] effective Hamiltonian $\mathcal{H}_i$ derived by Yosida[16] for a set of localized moments in a metal situated in a uniform magnetic field $\vec{H}$,

$$\mathcal{H}_i = \sum_n V_n^c + \mu_B \vec{H} \cdot \sum_n (\vec{L}_n + 2\vec{S}_n)$$
$$+ 2\mu_B J(0)\rho\vec{H} \cdot \sum_n \vec{S}_n - \sum_{n,m}' A_{nm}\vec{S}_n \cdot \vec{S}_m \ . \quad (2.1)$$

$\vec{L}_n$ and $\vec{S}_n$ are the orbital and spin angular momentum operators of an ion, V_n^c is the crystal-field potential, and μ_B is the magnitude of the electronic Bohr magneton. The zero-wave-vector component of the s-f coupling constant in $J(0)$, and ρ is equal to the conduction-electron density of state in energy per atom for one spin direction, or more generally, is proportional to the uniform Pauli spin susceptibility. The A_{nm} may in principle be obtained from the band structure, but in practice they are taken as adjustable parameters. The prime on the summation indicates that the $n = m$ terms are to be omitted.

The magnetization induced in the conduction electrons per ion is given by Yosida's[16] second equation

$$\langle \vec{m}_e \rangle_T = -\mu_B 2J(0)\rho \langle \vec{S} \rangle_T \ , \quad (2.2)$$

where we assume that there is only one magnetic atom per primitive cell. Because an angular momentum of $\tfrac{1}{2}\hbar$ corresponds to a spin magnetization of $-1\mu_B$, it follows that the angular momentum associated with Eq. (2.2) is $\hbar J(0)\rho\langle\vec{S}\rangle_T$.

The matrix material will also contribute to the magnetization and angular momentum. For example, its susceptibility χ_M will include the Pauli and orbital paramagnetic, and the Landau and core diamagnetic terms. The angular momentum will be proportional to $\chi_M\vec{H}/g_M'$, where g_M' is its experimentally determined gyromagnetic ratio.

The last term of Eq. (2.1) is treated by the mean-field method to give an exchange field $\vec{H}_e$ acting on each ion:

$$\vec{H}_e = J(0)\rho\vec{H} - \langle\vec{S}\rangle_T \mathcal{J}_{ff}/\mu_B \ , \quad (2.3)$$

where $\mathcal{J}_{ff} = \Sigma_n' A_{nm}$. The expression is valid in the paramagnetic and ferromagnetic regimes. This exchange field thus gives rise to a perturbation Hamiltonian $\mathcal{H}_p$,

$$\mathcal{H}_p = \mu_B(\vec{L} + 2\vec{S}) \cdot \vec{H} + \mu_B 2\vec{S} \cdot \vec{H}_e \ . \quad (2.4)$$

We now restrict the above equations to the case in which the separation between the multiplet levels is very large, so that only the contributions of the lowest one needs to be taken account of. The response of the matrix material is, in the remainder of this section, taken as being negligible compared to that due to the rare earths. We use the substitutions from the Wigner-Eckart theorem:

$$\vec{L} + 2\vec{S} \to g\vec{J}, \quad \vec{S} \to (g-1)\vec{J}, \quad \vec{L} \to (2-g)\vec{J}, \quad (2.5)$$

where $\vec{J} = \vec{L} + \vec{S}$. From these equations we may obtain the ionic magnetization per ion [Eq. (2.13 of I] to be

$$\langle m_i^z \rangle_T = -\mu_B \langle L^z + 2S^z \rangle_T \quad (2.6)$$

$$= H\chi_c(T)\frac{[1 + 2J(0)\rho(g-1)/g]}{1 - \lambda\chi_c(T)} \ . \quad (2.7)$$

The magnetic field H is applied along the z direction, which is one of the principal axes of the susceptibility, the molecular-field parameter λ is equal to $2\,\mathcal{J}_{ff}(g-1)^2/g^2\mu_B^2$, and $\chi_c(T)$ is the crystal-field susceptibility. This gives the response $\langle m_i^z \rangle_T = \chi_c(T)H$, as a function of temperature T, to a magnetic field and is calculated from a single-ion Hamiltonian of the form $V_c + \mu_B g J^z H$. Equations (2.5) then give

$$\langle J_i^z \rangle_T = -\frac{1}{g\mu_B} \frac{\chi_c(T)H[1 + 2J(0)\rho(g-1)/g]}{1 - \lambda\chi_c(T)} \ . \quad (2.8)$$

From Eq. (2.2) we obtain the angular momentum induced in the conduction electrons, and adding this to $\langle J_i^z \rangle_T$ we get the total angular momentum $\langle J_T^z \rangle_T$:

$$\langle J_T^z \rangle_T = - \frac{1}{g\mu_B} \frac{\chi_c(T)H[1+2J(0)\rho(g-1)/g][1+J(0)\rho(g-1)]}{1-\lambda\chi_c(T)} . \tag{2.9}$$

Now the total magnetic moment $\langle m_T^z \rangle_T$ was found in Eq. (2.18) of I to be

$$\langle m_T^z \rangle_T = \frac{\chi_c(T)H[1+2J(0)\rho(g-1)/g]^2}{1-\lambda\chi_c(T)} , \tag{2.10}$$

so the gyromagnetic ratio is

$$g' = \frac{g[1+2J(0)\rho(g-1)/g]}{1+J(0)\rho(g-1)}$$

$$\approx g[1+J(0)\rho(2-g)(g-1)/g] , \tag{2.11}$$

which is independent of the crystal-field splittings and of any temperature dependence of the molecular-field parameter.

For most of the heavy rare earths the quantity $(2-g)(g-1)/g$ is in the region $+0.15$, and as $J(0)\rho$ is about $+0.1$ in both the heavy[17] and light[7,12] rare-earth metals, the shift of gyromagnetic ratio is expected to be only 1 or 2%. Modern techniques[18,19] of measuring the gyromagnetic ratios of weakly paramagnetic metals have accuracies of about 5%, so they might not be capable of detecting the shift in the heavy rare-earth metals. The quantity $(2-g)(g-1)/g$ is a little larger in praeseodymium and neodymium, but in these cases the shift is small enough for it to be necessary to take into account the admixing of higher multiplet levels into the ground state by the applied and exchange fields, and also of the admixture of higher ionic terms by the spin-orbit interaction. This latter effect has the result of altering the g factor from the value given by the Landé formula. Samarium, though, has a value of $(g-2)(g-1)/g$, which is equal to -4.29, and we can therefore expect the gyromagnetic-ratio shifts to be very much larger in compounds containing this than in those containing other rare earths. However, in this case it is essential to take account of the admixture of the $J=\frac{7}{2}$ level into the $J=\frac{5}{2}$ ground state, as it is this effect which gives the temperature dependence of the gyromagnetic ratio. We examine this problem in Sec. III.

III. GYROMAGNETIC RATIOS OF SAMARIUM COMPOUNDS

In order to obtain a result which is algebraically concise, yet still physically useful, we make two approximations. The first is that only the lowest multiplet level of the samarium ion is thermally populated. This was found in I to restrict the applicability of the theoretical expression for the susceptibility to temperatures below about $230\,°K$, although it was argued that the expression for

$\langle S^z \rangle_T$, which is proportional to the excess Knight shift which is observed at the nucleus of a nonmagnetic atom, would be valid up to higher temperatures. Therefore we would expect the expression for g' derived in this section to become invalid as room temperature was approached, although the size of the error involved would depend upon the individual material. The second approximation is that there are no crystal-field splittings. Little is known about these splittings in metallic samarium materials, but there is an indication from calculations[20] of the splittings of the rare-earth series in the same cubic field, that the splittings of samarium tend to be the smallest in the series. It is also becoming clear[21] that the effect which the crystal field has of admixing the $J=\frac{7}{2}$ level into the $J=\frac{5}{2}$ ground state may have an important influence on the excess Knight shift. None the less, making use of these two approximations we obtain[7]

$$-\langle S^z \rangle_T = a[H+2H_e(g-1)/g](g-1)/gT + b(H+2H_e), \tag{3.1}$$

$$-\langle L^z + 2S^z \rangle_T = a[H+2H_e(g-1)/g]/T + b(H+2H_e), \tag{3.2}$$

where

$$a = \mu_B g^2 J(J+1)/3k , \tag{3.3}$$

$$b = 20\mu_B/7\Delta , \tag{3.4}$$

g and J refer to the lowest multiplet level, and $\Delta(=1550\,°K$, Refs. 2 and 6) is the separation between that and the $J=\frac{7}{2}$ one. The exchange field H_e is given by Eq. (2.3) and k is the Boltzmann constant. Equations (3.1) and (2.3) may then be solved to give $\langle S^z \rangle_T$ [Eq. (A11) of I]:

$$-\langle S^z \rangle_T/H = \left(1 - \frac{g}{(g-1)} \frac{T_\infty}{T_0}\right)$$

$$\times \left[b(1+2J(0)\rho) + \frac{g-1}{g} \frac{a}{(T-T_\infty)}\right]$$

$$\times \left(1 + \frac{2J(0)\rho(g-1)}{g} - [1+2J(0)\rho] \frac{T_\infty}{T_0}\right) , \tag{3.5}$$

where

$$T_0 = -(g-1)a/gb = 322\,°K , \tag{3.6}$$

$$T_\theta = 2\mathcal{J}_{ff}a(g-1)^2/g^2\mu_B, \tag{3.7}$$

and

$$\frac{T_\infty}{T_\theta} = 1 - \frac{g}{g-1} \frac{T_\infty}{T_0} . \tag{3.8}$$

Equation (3.5) may then be substituted into Eq. (3.2) to give

$$-\frac{\langle L^z + 2S^z\rangle_T}{H} = b\left(1 - \frac{g}{g-1}\frac{T_\infty}{T_0}\right)[1+2J(0)\rho]$$

$$+ \frac{a(1 - T_\infty/T_0)}{(T - T_\infty)}\left(1 + \frac{2J(0)\rho(g-1)}{g} - [1+2J(0)\rho]\frac{T_\infty}{T_0}\right).$$

$$(3.9)$$

This latter equation may be obtained by algebraic manipulation of Eq. (2.41) of I. In the case in which crystal-field splittings and the thermal population of higher multiplet levels must be taken account of, the two equations equivalent to (3.5) and (3.9) may be obtained by generalizing equations (3.1) and (3.2) to give the linear response of $\langle L^z + 2S^z\rangle_T$ and $\langle S^z\rangle_T$ to the fields H and H_e in this situation. The nonlinear responses to the fields may be used also to obtain the spontaneous moments of an ordered system by solving Eq. (2.3) and the nonlinear generalization of Eq. (3.1) self-consistently. It can be seen from Eq. (3.8) that if the ratio T_θ/T_0 exceeds a certain value then T_∞ will diverge and the system will become ordered at ar-

bitrary finite temperatures. This is discussed further in Appendix B.

Subtracting Eq. (3.5) from (3.9) we obtain the angular momentum of the $4f$ shell:

$$-\frac{\langle L^z + S^z\rangle_T}{H}$$

$$= \frac{1}{g}\frac{a\{1+2J(0)\rho(g-1)/g-[1+2J(0)\rho]T_\infty/T_0\}}{T - T_\infty},$$

$$(3.10)$$

and for the sake of completeness we write down the remaining equation

$$\frac{-\langle L^z\rangle_T}{H} = -b\left(1 - \frac{g}{g-1}\frac{T_\infty}{T_0}\right)[1+2J(0)\rho]$$

$$+ \frac{a[(2-g)/g + T_\infty/T_0]}{T - T_\infty}$$

$$\times\left(1 + \frac{2J(0)\rho(g-1)}{g} - [1+2J(0)\rho]\frac{T_\infty}{T_0}\right).$$

$$(3.11)$$

Then, combining Eqs. (3.10), (3.5), and (2.2) we obtain the total angular momentum of the material per magnetic atom

$$\frac{-\langle J_T^z\rangle_T}{H} = \chi_M/g'_M\mu_B + J(0)\rho b[1+2J(0)\rho]\left(1 - \frac{g}{g-1}\frac{T_\infty}{T_0}\right)$$

$$+ \frac{a\{1+2J(0)\rho(g-1)/g-[1+2J(0)\rho]T_\infty/T_0\}[1+J(0)\rho(g-1)-gJ(0)\rho T_\infty/T_0]}{g(T - T_\infty)}. \qquad (3.12)$$

For elemental samarium, the properties of the matrix, χ_M and g'_M, might be expected to correspond to those of lanthanum ($4f^0$), because it was found in I that the susceptibility of lanthanum corresponded much better to the matrix susceptibility of samarium than did that of lutetium ($4f^{14}$). Curiously, although lanthanum has almost the same specific-heat density of states as lutetium[22,23] its susceptibility is five times higher.[24]

The total magnetization $\chi_T(T)H$ was found previously [Eq. (2.42) of I] to be given by

$$\frac{\chi_T(T)}{\mu_B} = \frac{\chi_M}{\mu_B} + b\left(1 - \frac{gT_\infty}{(g-1)T_0}\right)[1+2J(0)\rho]^2$$

$$+ \frac{a\{1+2J(0)\rho(g-1)/g-[1+2J(0)\rho]T_\infty/T_0\}^2}{T - T_\infty}.$$

$$(3.13)$$

It is interesting to note that the magnetic quantities of importance, Eqs. (3.5), (3.9), and (3.10)–(3.13) may all be expressed as the sum of a temperature-independent term plus a Curie–Weiss term. The numerator of the Curie–Weiss term of only Eq. (3.13) is a perfect square, as it must be to pro-

vide the positive total paramagnetic susceptibility for all values of the parameters, which is required by thermodynamics.[25] By dividing the expression given by Eq. (3.13) by that given by Eq. (3.12) we obtain the gyromagnetic ratio g'. We now attempt to estimate the size of this in metallic samarium materials.

As an example, we use the parameters which were deduced in I from the analysis of the paramagnetic susceptibility of rhombohedral samarium metal. Although the neutron diffraction experiments of Koehler and Moon[11,12] have revealed that the analysis was invalid, because $\frac{2}{3}$ of the atoms order magnetically at 106 °K (this possibility had been anticipated in I; a further discussion is given in Appendix A of the present paper), we use these parameters to obtain an estimate of the magnitude of the effects which might be expected in a roughly similar material, mainly because the size of the most significant parameter $J(0)\rho$ is +0.123. This is midway between the value of +0.10 obtained from the analysis in I of the paramagnetic susceptibility of double-hexagonal close-packed samarium and the value of +0.15 which Koehler and Moon[12] esti-

mated from an analysis of the magnetic form factor of the cubic sites in rhombohedral samarium.

The susceptibility of rhombohedral samarium could be fitted from 15 to 230 °K by the relation[7]

$$\chi_T(T) = [7.838 + 106.8/(T + 9.46)] \times 10^{-6} \text{ emu/g}. \tag{3.14}$$

From Eqs. (3.3) and (3.4) we obtain $aN^*\mu_B = 594 \times 10^{-6}$ emu/g and $bN^*\mu_B = 4.61 \times 10^{-6}$ emu/g, where N^* is the number of atoms per gram, and from these the parameters $T_\theta = -9.6$ °K, $J(0)\rho = +0.123$, $\chi_M = 0.78 \times 10^{-6}$ emu/g. If we then take g_M' to be 2 we can calculate the angular momentum of Eq. (3.12) to be

$$- \langle J^z \rangle_T / H = \mu_B^{-1}[1.084 + 804/(T + 9.46)] \times 10^{-6} \text{ emu/g}, \tag{3.15}$$

and so

$$g' = [7.838 + 106.8/(T + 9.46)]$$
$$\times [1.084 + 804/(T + 9.46)]^{-1}. \tag{3.16}$$

This is plotted as the continuous line in Fig. 1. The dashed line is the value of g' for the noninteracting ion, $g' = g(1 + 2.5T/T_0)$. The values calculated by Frank[1] and Van Vleck,[2] which take account of the thermal population of higher-multiplet levels, but of no interactions, are indistinguishable
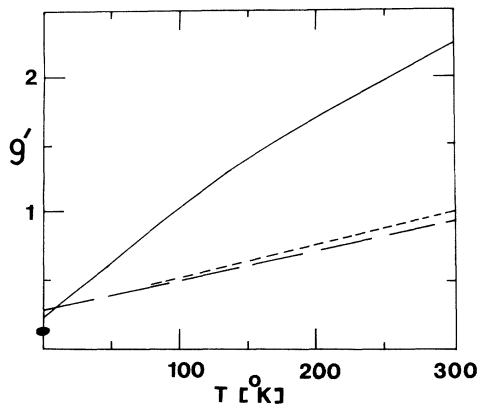

FIG. 1. Results of a calculation of the gyromagnetic ratio g', as a function of temperature, of a paramagnetic metallic samarium material in which the interactions are of a size comparable to those which exist in samarium metal. The continuous line gives the values calculated using the exchange interactions and conduction-electron polarization effects discussed in the text. The dashed line gives the value for noninteracting samarium in which only the lowest multiplet level is thermally populated. The dotted line is for noninteracting samarium plus a matrix material which has a susceptibility of 0.75×10^{-6} emu/g and a gyromagnetic ratio g_M' of 2. The dot shows g' at 0 °K for the ferromagnetic state of the material with interactions, assuming no crystal-field splittings and no nuclear polarization. The spin-orbit screening constant σ has been taken to have a value of 33 in the calculation.

from those given by the dashed line below 300 °K. In order to estimate the influence of the matrix properties we have also calculated g' for a material with the same atomic density as elemental samarium, and having no interactions, but with a matrix susceptibility of 0.75×10^{-6} emu/g and a g_M' of 2 (although recent experiments[19] on other transition metals show that g_M' is often significantly less than 2). This calculation is shown as the dotted line in Fig. 1. There is little difference between this and the dashed line, which suggests that, for the sizes of the parameters considered here, these matrix properties do not have too great an effect upon the total gyromagnetic ratio. It is seen that there is a large difference between the bare gyromagnetic ratios and the value calculated when taking account of interactions; the difference is nearly a factor of 2. This is primarily due to the influence of conduction-electron polarization.

The gyromagnetic ratio of the material in the ferromagnetic phase may be calculated by using the method of Ref. 10 and evaluating the expectation values of the spontaneous angular momentum and magnetic moment.[26] If there are no crystal-field splittings it is straightforward to show that in zero applied field at 0 °K, g' is given by

$$g' = \frac{2[1 - 0.900T_\theta/T_0 - 5J(0)\rho]}{7[1 - 0.257T_\theta/T_0 - 0.714J(0)\rho]}, \tag{3.17}$$

and putting in the values obtained from Eq. (3.14) we obtain $g' = 0.128$. This is shown as the dot in Fig. 1. It illustrates further the wide range of values of the gyromagnetic ratio which might be found in a single metallic samarium compound, although, of course, we know that, in reality, this particular material would order antiferromagnetically because T_∞ is negative. At very low temperatures, though, the hyperfine field would polarize the nuclear spins, and this could give a significant contribution to the angular momentum of the solid.

IV. CONCLUSIONS

It has been shown how the conduction-electron spin polarization, which is induced by the s-f interaction, changes the gyromagnetic ratios of non-S-state metallic rare-earth materials. The shift in gyromagnetic ratio is found to be of the order of a few percent for the rare-earth metals apart from samarium, too small to be measured accurately by present experimental techniques.[18,19] However, a calculation of the effect in a metallic samarium material, in which the interactions are of a size comparable to those which are known to exist in elemental samarium, suggests that the shift might be very large and positive, perhaps of the order of 100%. Measurements of the temperature dependence of the gyromagnetic ratio of samarium metal might provide valuable help in interpreting its mag-

netic properties.

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APPENDIX A

At the time when Paper I was written there seemed to be some ambiguity in the published experimental data[27] as to whether rhombohedral samarium ordered magnetically at 106 °K. Since then, the neutron diffraction experiments of Koehler and Moon[11,12] have confirmed that at this temperature $\frac{2}{3}$ of the atoms, those on the hexagonal sites, order antiferromagnetically. Therefore, the analysis given in I of the susceptibility of rhombohedral samarium is invalid, because it assumed that the material remained in the paramagnetic state down to 15°K. This ambiguity of the data, and the possibility that the analysis might be invalid, has been noted and forseen in our original paper.[7]

However, the susceptibility measurements[28] which were analyzed, appeared to obey the Curie–Weiss law of Eq. (3.14) rather well above 15 °K, so it is interesting to inquire if any useful information may be extracted from them. In fact, the points between 15 and 100 °K may be fitted to an accuracy of 0.5% by

$$\chi(T) = [7.853 + 98.96/(T + 6.70)] \times 10^{-6} \text{ emu/g} ,$$

(A1)

the greater accuracy being obtained from the need to fit fewer points.

This expression may be analyzed in the same manner as in I if the assumption is made that the temperature dependence is due entirely to the $\frac{1}{3}$ of the ions on the cubic sites which have not ordered.[29] (In other words, the $\frac{2}{3}$ on the hexagonal sites which have ordered are assumed to give only a temperature-independent contribution to the susceptibility.) On this basis we obtain the results $J(0)\rho = +0.063$, $T_\theta = -6.8$ °K, and that the temperature-independent component of the susceptibility which arises from the atoms on the hexagonal sites is 5×10^{-6} emu/g, excluding the matrix contribution. It is hard to assess the significance of the latter two results, but $J(0)\rho$ is at least of the same sign and magnitude as the value of $+0.15$ estimated by Koehler and Moon.[12]

However, a complication which we have ignored is that the $\frac{2}{3}$ of the ions which have ordered produce a molecular field which acts on the $\frac{1}{3}$ which have not. This molecular field will be zero when half of the spins on the hexagonal sites point in one direction and the other half point in the opposite direction, as has been proposed by Koehler and Moon,[11] but it need not be zero when the magnetization of each of the halves of the hexagonal sites has a component in the same direction, as it will when a magnetic field is applied. This molecular field will then be proportional to the applied field, and because it acts on the 4f spin it may make itself manifest as a contribution to $J(0)\rho$, as may be seen from Eq. (2.3). This may be the explanation of why the $J(0)\rho$ we find is not the same as the $+0.15$ of Koehler and Moon. On the other hand, the magnetization of the cubic sites will exert a molecular field on the hexagonal sites, and in a complete theory this must be taken account of in a self-consistent manner. Furthermore, it is doubtful if the neglect of crystal-field effects can be justified at such low temperatures. It is probable that substantial progress in sorting out the various contributions to the susceptibility of rhombohedral samarium, both below and above 106 °K, will not be made until the natures of these crystal-field levels and their splittings are fully known.[30]

APPENDIX B

Equation (3.8) may be rearranged to give

$$\frac{T_\theta}{T_\infty} = 1 + \frac{g}{g-1} \frac{T_\theta}{T_0} ,$$

(B1)

and it follows that if

$$T_\theta > -(g-1) T_0/g = 805 \text{ °K} ,$$

(B2)

then the susceptibility will diverge at finite temperature, in the sense that T_∞ will become infinite; this corresponds to the spontaneous admixing of the $J = \frac{7}{2}$ level into the $J = \frac{5}{2}$ ground state. The ordered state would be broken up at higher temperatures as higher-lying multiplet levels became thermally populated. The condition (B2) may be formulated in a different way if it is recalled that

$$T_\theta = 2(g-1)^2 J(J+1) \mathcal{J}_{ff}/3k .$$

(B3)

The factor $(g-1)^2 J(J+1)$ is 4.46 for the ground state of samarium and 15.75 for gadolinium. Therefore, if a gadolinium compound could be found with an ordering temperature of greater than (805 °K) × (15.75/4.46) = 2840 °K, and the gadolinium substituted by samarium then, other things being equal, this spontaneous polarization would occur. However, this temperature is an order of magnitude greater than the highest known ordering temperatures of gadolinium compounds,[31] so the effect is not likely to be found in practice.

It is known[32] that an analogous effect can occur in compounds containing tripositive europium ($4f^6$) which has a $^7F_0$ ground state with a $^7F_1$ level Δ (≈ 530 °K[6]) above it. At 0 °K the susceptibility associated with the rare-earth ions will be given[33] by the second term of Eq. (3.13),

$$\chi = \frac{8\mu_B^2}{\Delta} \frac{[1 + 2J(0)\rho]^2}{1 - 16\mathcal{J}_{ff}/\Delta} , \tag{B4}$$

which will diverge when $\mathcal{J}_{ff} = \frac{1}{16}\Delta$. Making use of Eq. (B3) the criterion is obtained that if a gadolinium compound can be found with an ordering temperature of greater than 350 °K, and if the gadolinium can be substituted by trivalent europium (europium though, has an unfortunate tendency to become divalent), then, within the validity of the mean-field model, the europium will become magnetically ordered by a polarization instability of the ground state. This argument is valid for types of ordering other than ferromagnetic. There is

considerable current interest in the elementary excitations of such systems,[34] but 350 °K seems tantalizingly just out of reach.[31] However, compounds might be found in which the exchange was strong enough to cause some observable dispersion in the excitation spectra.

The gyromagnetic ratio of a paramagnetic tripositive europium compound at 0 °K is given by

$$g' = [1 + 2J(0)\rho]/J(0)\rho , \tag{B5}$$

but in this case the matrix would have an important influence, as its contributions would probably be comparable to those due to the rare-earth ions.

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[1]A. Frank, Phys. Rev. **39**, 119 (1932).

[2]J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford U. P., London, 1932).

[3]S. P. Heims and E. T. Jaynes, Rev. Mod. Phys. **34**, 143 (1962).

[4]C. J. Gorter and B. Kahn, Physica **7**, 753 (1940).

[5]W. M. Lomer, Proc. Phys. Soc. **91**, 933 (1967).

[6]G. H. Dieke, *Spectra and Energy Levels of Rare Earth Ions in Crystals* (Interscience, New York, 1968).

[7]A. M. Stewart, Phys. Rev. B **6**, 1985 (1972). The subject matter of this paper was presented at the First European Conference on the Physics of Condensed Matter; Florence, Italy: and at the Conference on Dilute Alloys; Tihany, Hungary: both in September, 1971. Preliminary steps towards the solution of the problem had been made in the author's Ph.D. thesis (University of London, 1971).

[8]A. M. Stewart, J. Phys. F: Metal Physics **2**, L44 (1972). The giant moment of SmPd predicted in this paper was based upon the severely reduced paramagnetic moment which D. Shaltiel, J. H. Wernick, H. J. Williams and M. Peter [Phys. Rev. **135**, A1346 (1964)] found in GdPd. However, R. P. Guertin, H. C. Praddaude, S. Foner, E. J. McNiff and B. Barsoumian [Phys. Rev. B **7**, 274 (1973)] found that a 1% GdPd alloy possessed a paramagnetic moment which was very close to the free-Gd-ion value. If this latter result is accepted, then the giant moment of SmPd should not exist.

[9]A. M. Stewart, J. Phys. F: Metal Physics **3** 1024 (1973).

[10]A. M. Stewart, Phys. Stat. Sol. (b) **52**, K1 (1972). The magnetization m associated with a normal rare earth without crystal-field splittings is given, generally, by $m = m_0 B_J((m_0/kT)\{H + \lambda m[1 + 2J(0)\rho(g-1)/g]^{-2}\})$, where $m_0 = \mu_B g J[1 + 2J(0)\rho(g-1)/g]$ and $B_J\{x\}$ is the Brillouin function. However, it may be difficult to find a system for which this expression is adequate. Even gadolinium has crystal-field splittings of about 1 °K [B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (Interscience, New York, 1965)]. This may explain why the magnetization measurements made on GdPd by the authors referred to in Ref. 8 (Guertin *et al.*) did not follow a Brillouin curve. Clustering effects may have had an influence as well.

[11]W. C. Koehler and R. M. Moon, Phys. Rev. Letters **29**, 1468 (1972).

[12]R. M. Moon and W. C. Koehler, in 18th Annual Conference on Magnetism and Magnetic Materials, Denver 1972 (unpublished).

[13]S. Arajs and R. V. Colvin, in *Rare Earth Research*, edited by J. F. Machman and C. E. Lundin (Gordon and Breach, New York, 1962).

[14]S. Arajs and R. V. Colvin, in *Rare Earth Research*, edited by E. V. Kleber (Macmillan, New York, 1961); S. Arajs, Phys. Rev. **120**, 756 (1960).

[15]It should be pointed out that this *static* effective Hamiltonian is still being used to interpret *dynamical* properties, such as spin-wave spectra. It is possible that a theoretically more valid approach is required.

[16]K. Yosida, Phys. Rev. **106**, 893 (1957).

[17]T. Kasuya, in *Magnetism IIB*, edited by G. T. Rado and H. Suhl (Academic, New York, 1966).

[18]R. Huguenin and D. N. Baldock, Phys. Rev. Letters **16**, 795 (1966).

[19]R. Huguenin, G. P. Pells, and D. N. Baldock, J. Phys. F: Metal Phys. **1**, 281 (1971).

[20]J. A. White, J. Phys. Chem. Solids **23**, 1787 (1962).

[21]S. K. Malik and R. Vijayaraghavan, Phys. Letters 34A, 67 (1971); J. Phys. (Paris) **32**, C1-1028 (1971). H. W. de Wijn, A. M. van Diepen, and K. H. J. Buschow, Phys. Rev. B **7**, 524 (1973). It is interesting to note that the two samarium compounds having anomalous "anomalous" Knight shifts, which were discussed by the latter authors, both have susceptibilities which are substantially constant above 300 °K, whereas the susceptibilities of normal samarium compounds increase above this temperature.

[22]O. V. Lounasmaa and M. C. Veuro, Phys. Lett. 40A, 371 (1972).

[23]It is interesting to note that specific-heat density of states of samarium was found in Ref. 22 to be greater than that of lanthanum. This indicates, partially, why the $J(0)\rho$ of the cubic sites of rhombohedral samarium, found in Ref. 12, is so large.

[24]F. H. Spedding, S. Legvold, A. H. Daane, and L. D. Jennings, in *Progress in Low Temperature Physics*, edited by G. J. Gorter (North-Holland, Amsterdam, 1957), Vol. 2.

[25]It is possible for the 4f shell magnetization or the conduction electron magnetization, whichever is the smaller, to be negative when $J(0)$ is positive. The sum of them must, of course, be positive. See Ref. 8.

[26]Note that $\langle L^z + S^z \rangle = M$ in Ref. 10, when the admixture is small enough to be treated by first-order perturbation theory.

[27]The author was then unaware of the susceptibility measurements of S. Arajs and G. R. Dunmyre, Z. Naturforsch. 21A, 1856 (1966), which showed a small but distinct peak at 108 °K.

[28]A. Jayaraman and R. C. Sherwood, Phys. Rev. 134, A691 (1964).

[29]This suggestion is due to A. R. Mackintosh (comment made at Conference on Physics of Condensed Matter, Florence 1971).

[30]This does not imply that the Ruderman-Kittel-Kasuya-Yosida free-electron model is applicable. Although we think that an effective Hamiltonian of the form of Eq. (2.1) is substantially valid, the details of the inter-actions will be more complicated. See I. A. Campbell, J. Phys. F: Metal Phys. 2, L47 (1972); B. R. Coles, D. Griffiths, R. J. Lowin, and R. H. Taylor, J. Phys. C: Solid State Phys. 3, L121 (1970); A. A. Gomes, A. P. Guimarães, and L. Iannarella, J. Phys. C: Solid State Phys. 5, L99, (1972). A theory with similarities to that of Gomes, et al. had been put forward by the author: A. M. Stewart, Ph.D. thesis, 1971, University of London (unpublished).

[31]K. N. R. Taylor, Adv. Phys. 20, 551 (1971).

[32]R. M. Bozorth and J. H. Van Vleck, Phys. Rev. 118, 1493 (1960).

[33]Using the expression for b given by Eq. (2.31) of Ref. 7 with $J = 0$.

[34]P. Fulde and I. Peschel, Adv. Phys. 21, 1 (1972).