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Paramagnetic Susceptibilities of Metallic Samarium Compounds

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It is shown that the influence of conduction-electron polarization effects upon the susceptibilities of metals containing the tripositive samarium ion is very much greater than upon metals containing normal rare earths. A theory of the susceptibility of metallic samarium materials is developed which takes account of these polarization effects and of interionic Heisenberg exchange couplings, the admixture of the $J=\frac{7}{2}$ state into the $J=\frac{5}{2}$ ground state, which is assumed to be the only one to be thermally populated, but which, however, does not take account of crystal-field splittings. The susceptibility is found to be of the unexpectedly simple form $\chi(T)=\chi_0+D/(T-\theta)$, in which the only dependence on temperature T is that explicitly shown. This expression is found to fit the published data for the susceptibility of dhcp samarium to an accuracy of 1% in the temperature region 110–230 °K, and the parameters extracted from the fit are found to be in excellent agreement with those obtained for the other light rare-earth metals. An expression is also derived for the susceptibilities of metals containing normal rare earths, which takes account of both conduction-electron polarization and crystal field effects.

I. INTRODUCTION

The purpose of this paper is to direct attention to the effects of conduction-electron spin polarization upon the paramagnetic susceptibilities of metallic rare-earth compounds, in particular those containing samarium. Although for "normal" rare-earth ions (that is, those whose properties may be adequately described by taking account only of the lowest angular momentum level of quantum number J) the effects of conduction-electron spin polarization upon the paramagnetic susceptibility are rather small—of the order of a few percent—they are nonetheless important to measure because from them the *sign* of the coupling constant between the f shell and the conduction electrons may be deduced.[1] The sign of this quantity, which is believed to consist of a positive contribution from direct exchange[2] and a negative contribution from s-f mixing,[3] is difficult to obtain by other means. Measurements of the ESR g shift[4] should give it directly, but in practice resonances are rarely seen for other than S-state ions, and when they are seen, bottleneck effects[5] make their interpretation difficult. The excess Knight shift at a nonmagnetic nucleus in a rare-earth compound can in principle give the sign,[6] but a detailed knowledge of the compound's band structure is needed to calculate it, and our present knowledge of band structures is inadequate for this purpose. The sign may also be deduced from logarithmic anomalies in the resistivity,[7,8] but only if they are large enough to be detectable, and for rare-earth materials apart from those in the virtual-bound-state category, they usually are not.

It is recognized that the effect of conduction-electron polarization upon the susceptibilities of metals containing normal rare earths is small; however, the effect of it upon metals containing samarium, as we shall show in this paper, is very much larger. In fact, in order to attempt to understand the paramagnetic susceptibility of elemental samarium metal it is essential to take account of conduction-electron polarization, and this aspect of the problem has not been adequately treated before. In this paper we therefore calculate expressions for the susceptibilities of metallic compounds containing samarium or normal rare earths which take account of this important feature.

The free-tripositive samarium ion possesses five electrons in its $4f$ shell and has a spectroscopic structure which is well described by Hund's rules. The lowest term is a ^6H ($S=\frac{5}{2}$, $L=5$, where S and L are the spin and orbital angular momentum quantum numbers, respectively), and this is split by the spin-orbit interaction into a multiplet with a $J=\frac{5}{2}$ ground state. The first excited level, the $J=\frac{7}{2}$, lies about $\Delta=1550$ °K above it,[9] and the other angular momentum levels are correspondingly higher. The effective paramagnetic moment of the $J=\frac{5}{2}$ ground level, which is given by $g[J(J+1)]^{1/2}$, where g is the Landé factor of that level, happens to be rather small ($0.845\mu_B$) compared to those of the other rare earths apart from europium. The consequence of this is that a large portion of the magnetic susceptibility of an assembly of free samarium ions will arise from the virtual transitions between the $J=\frac{5}{2}$ level (which throughout this paper we assume to be the only one to be thermally populated) and the $J=\frac{7}{2}$ level, which are induced by the applied magnetic field. The susceptibility will then be proportional to $b+a/T$, where T is the temperature. This expression for the susceptibility and its generalization to take into account the thermal population of higher J levels was first obtained by Van Vleck,[9] and the term b and the transitions which give rise to it are known as the Van Vleck term and the Van Vleck transitions, respectively.

When the magnetic ion is situated in a metal, it is subjected to two main influences. The first is the effect of so-called crystal fields which split the $2J+1$ degenerate states of each angular momentum level into a number of levels which depends upon the point symmetry of the solid about the magnetic site. The crystal fields will also admix angular momentum levels, but this effect is not expected to be big enough to influence substantially the susceptibility behavior of the normal rare earths; it may, however, affect samarium materials.[10] The magnitudes of these fields are difficult to calculate from first principles, particularly in metals,[11] but once they are known or taken as given parameters, their effects upon rare-earth ions may be calculated by the concise methods of Stevens[12] and Elliott and Stevens.[13] The second influence which acts upon the ion is the s-f coupling between the ion and the conduction electrons, which may be written in the schematic form $-2\mathcal{J}_{sf}\vec{S}\cdot\vec{s}$, where $\vec{S}$ is the spin operator of the magnetic ion, $\vec{s}$ is that of a conduction electron, and $\mathcal{J}_{sf}$ is the coupling constant which is a matrix element depending in general upon the initial and final wave vectors of the scattered conduction electron.[2] This gives rise first to a long-range Heisenberg coupling between ionic spins and second to a clothing of the bare rare-earth spin with a conduction-electron cloud which adds or subtracts a portion of conduction-electron spin magnetization to the free-ion moment. These effects are associated with the names of Ruderman and Kittel,[14] Kasuya,[2] and Yosida,[4] known collectively as RKKY.

Therefore in a calculation of the susceptibility of a system of rare-earth ions in a metallic solid, the following factors must be taken into account: (a) the crystal-field splittings of each J level and the admixture of one with another; (b) RKKY Heisenberg interactions between ions; (c) Van Vleck transitions between different J levels which are caused both by the applied magnetic field and by the exchange fields when the RKKY interactions are treated in a molecular-field approximation; (d) the effects of the conduction-electron spin polarization clothing of the bare-ion spin; and (e) the thermal population of higher-lying J levels.

A susceptibility calculation has not yet been made for any rare-earth material which takes account of all five of these factors. Van Vleck[9] made calculations which considered (c) and (e), and Frank[15] considered (a), (c), and (e) together. De Wijn *et al.*[16] derived an expression for the susceptibility of a samarium compound taking account of factors (b), (c), and (e). They treated the Heisenberg exchange interactions by means of the molecular-field method put forward by Wolf and Van Vleck[17] and also obtained an expression for the quantity $\langle S^z \rangle_T / H$, where $\langle S^z \rangle_T$ is the thermal average of the ionic operator S^z, z being the direction of the applied magnetic field H. Bleaney[18] took account of (a) and (b) and derived the following equation for the susceptibility $\chi(T)$:

$$\chi^{-1}(T) = \chi_c^{-1}(T) - \lambda \ , \tag{1.1}$$

where $\chi_c(T)$ is the susceptibility of the noninteracting system of ions subject to the crystal field and λ is the molecular-field parameter. This equation is valid only within the manifold of states of the lowest J level.

As for the effects of conduction-electron polarization upon the susceptibility, it is known[1] that if the susceptibility of a system of bare ions is a'/T, then the full susceptibility is given by

$$\chi(T) = \frac{a'[1 + 2J(0)\rho(g-1)/g]^2}{T - \lambda a'} \ . \tag{1.2}$$

This equation takes account of factors (b) and (d). $J(0)$ is the $\vec{q} = 0$ component of the wave-vector-dependent coupling constant $J(\vec{q})$ which appears in Kasuya's second-quantized formulation of the s-f interaction. For an electron gas in which there are no internal exchange or Coulomb interactions, ρ is equal to the conduction-electron density of states per atom at the Fermi surface for one spin direction. This notation is the same as Kondo's.[8] For a free-electron gas, ρ is given by

$$\rho = 3Z/4E_F \ , \tag{1.3}$$

where E_F is the Fermi energy and Z is the average number of conduction electrons per atom in the metal. It is recognized, though,[19] that even for an interacting electron gas, ρ is proportional to the uniform Pauli spin susceptibility,

$$\rho = \chi_g / 2\mu_B^2 N^* \ , \tag{1.4}$$

where χ_g is the Pauli spin susceptibility per unit mass, μ_B is the magnitude of the electronic Bohr magneton, and N^* is the total number of atoms (including both magnetic and nonmagnetic ones) per unit mass. The susceptibility of the metallic matrix χ_M, which consists of the Pauli and orbital paramagnetic and the Landau and core diamagnetic contributions, and which is usually substantially temperature independent, must be added onto the right-hand side of Eq. (1.2) in order to obtain the total susceptibility of the solid.

Another interesting property of the paramagnetic state of metallic rare-earth compounds is the excess Knight shift which occurs at the nuclei of the nonmagnetic atoms. This arises because the s-f interaction allows the magnetic atoms to polarize the conduction electrons in their vicinity and so propagate waves of spin density through the crystal. These impinge upon the nuclei of the nonmagnetic atoms, which sense them through their hyperfine interaction. This excess Knight shift, which is the Knight shift in addition to that caused by the normal uniform conduction-electron polarization mechanism, is proportional to $\langle S^z \rangle_T / H$.[4] For the normal rare earths apart from tripositive samarium and europium, $\langle S^z \rangle_T$ is proportional to the ionic magnetization $-\mu_B \langle L^z + 2S^z \rangle_T$, and hence the excess Knight shift is proportional to the ionic susceptibility. However, for samarium Van Vleck transitions play an important part, and it has been shown by White and Van Vleck[20] that because of this the excess Knight shift in samarium compounds should change sign at about 300 °K. De Wijn *et al.*[16] reported that their calculated expression for $\langle S^z \rangle_T / H$ was reasonably similar to the experimental values of excess Knight shift which they obtained for the compound $\mathrm{SmAl_3}$ and that their calculated susceptibility also resembled the experimental results. However, a measurement of the excess Knight shift of $\mathrm{SmAl_2}$[21] failed to reveal any change of sign, and Malik and Vijayaraghavan[10] have suggested that in this compound crystal fields may play an important part by mixing higher J levels into the $J = \frac{5}{2}$ ground state, thus preventing the crossover.

The plan of the remainder of this paper is as follows. In Sec. II A we discuss the effective Hamiltonian for the magnetic ions, which is our starting point for calculations of the magnetic properties of rare-earth materials. It contains the effects of crystal fields and the effects of conduction-electron polarization obtained from treating the s-f interaction to second order in perturbation theory. Heisenberg exchange interactions are treated in the molecular-field approximation. Whether or not Van Vleck transitions between different J levels are taken account of depends on which manifolds of states the effective Hamiltonian is allowed to act upon. In Sec. II B the Hamiltonian is solved within the manifold of states of a single J level, and a generalization of Bleaney's[18] equation (1.1) is obtained which is valid for a metal. In Sec. II C the effective Hamiltonian is applied to a set of ionic states which, it is hoped, will adequately represent the samarium ion. Van Vleck transitions are allowed but crystal-field splittings are taken to be zero. In addition, it is assumed that only the lowest J level is thermally populated. The results should therefore be applicable to samarium in a temperature range above that at which crystal-field splittings have a significant effect upon the susceptibility and below that at which the thermal population of higher J levels becomes important. In Sec. III the theories are compared with published experimental data for some of the light rare-earth metals.

II. THEORY

A. Effective Hamiltonian

The s-f or s-d Hamiltonian[22] is notoriously difficult to handle, and it was not until 1957 that Yosida[4] fully calculated the effects of it to the lowest orders of perturbation theory. Kondo[7] began the investigation of the consequences of treating the interaction to higher order, and the question of what happens to a local moment at low temperature when the s-d interaction is treated fully, particularly when the coupling constant is negative, is still far from settled.[8]

In this paper we only consider the effect of the s-f interaction to the lowest orders in perturbation theory. Therefore we take as the starting point of our calculation the effective Hamiltonian $\mathcal{H}_i$ for the magnetic ions which was derived by Yosida.[4] This is

$$\mathcal{H}_i = \sum_n V_n^c + \mu_B H \sum_n (L_n^z + 2 S_n^z) + \mu_B H J(0) \rho \sum_n 2 S_n^z - \sum_{\substack{n,m \\ n \neq m}} A_{nm} \vec{S}_n \cdot \vec{S}_m \,. \tag{2.1}$$

Yosida also obtained an equation relating the total spin polarization in the conduction band $(n_\uparrow - n_\downarrow)$ (the total number of conduction electrons with spin-up minus the number with spin-down) to the ionic spin operators:

$$n_\uparrow - n_\downarrow = J(0)\rho \textstyle\sum_n 2 S_n^z \,. \tag{2.2}$$

This conduction-electron spin polarization is not, of course, uniform throughout the metal. It is distributed in the well-known RKKY magnetization density oscillations originating from each magnetic ion. H is the magnetic field, which is in the z direction, L^z and S^z are the operators for the z component of the orbital and spin angular momenta, respectively, of the magnetic ions, and $J(0)$ and ρ have been defined previously. The coefficients A_{nm}, which give the strength of the exchange couplings between the ions, depend on the detailed nature of the metal's band structure and of the s-f coupling. The general expression for them has been given by Yosida,[4] who has calculated analytical forms for them using certain simplifying assumptions. Their exact forms need not concern us here; we shall take them as adjustable parameters.

In transferring Eqs. (2.1) and (2.2) from Yosida's paper we have made several changes in them. We have omitted terms which refer to nuclear interactions, which are not relevant to the problems considered here. We have also omitted a term from each equation which refers to the uniform Pauli conduction-electron spin polarization of the metal; this must be added on at the end of the calculation in order to obtain the total magnetization of the solid. The quantity $(aN)^{-1}$ of Yosida[4] has been converted by Eq. (1.3) into 2ρ, and also the terms $n=m$ have been omitted from the double summation. This omission will be justified in Sec. II B. To Yosida's Hamiltonian we have added a term $\mu_B L^z H$ which represents the interaction of the orbital part of the ion's angular momentum with the applied magnetic field. A Hamiltonian V_n^c which represents the potential energy of the ionic electrons in the crystal field has also been formally added.

We may now treat the term in Eq. (2.1) which contains the Heisenberg exchange interactions by a molecular-field method,[17] which applies in the paramagnetic and ferromagnetic regimes, and reduce it to

$$-2\mathcal{J}_{ff} \langle S^z \rangle_T \sum_n S_n^z \,, \tag{2.3}$$

where

$$\mathcal{J}_{ff} = \sum_{\substack{n \\ n \neq m}} A_{nm} \,. \tag{2.4}$$

If we substitute Eq. (2.3) into (2.1) the following single-ion Hamiltonian is obtained:

$$\mathcal{H} = V_c + \mu_B (L^z + 2S^z) H + \mu_B 2 S^z [J(0)\rho H - \langle S^z \rangle_T \mathcal{J}_{ff} / \mu_B] \,. \tag{2.5}$$

In the interests of simplicity we have assumed that the compound whose susceptibility we shall calculate has only one magnetic atom per primitive cell, although elemental samarium has more, and even though it is known that anisotropic[23] and non-Heisenberg[24] exchange effects may be important in some circumstances, we shall not consider them in any detail, but only take account of the isotropic Heisenberg interionic interactions which result from the simple RKKY mechanism.

In the remainder of Sec. II this effective Hamiltonian will be applied to two situations which are of importance for rare-earth magnetic materials, with the purpose of obtaining $\langle S^z \rangle_T$, which determines the excess Knight shift, the ionic magnetization per ion

$$m^i = -\mu_B \langle L^z + 2 S^z \rangle_T \,, \tag{2.6}$$

and the magnetization per ion m^e of the electron gas, which from Eq. (2.2) is given by

$$m^e = -\mu_B 2 J(0) \rho \langle S^z \rangle_T \,. \tag{2.7}$$

The sum of $m^i + m^e$ then gives the "dressed" magnetization of the ion.

B. Susceptibility of Materials Containing Normal Rare-Earth Ions

We now proceed to solve the effective Hamiltonian within a manifold of states of constant J. This should accurately represent the situation for normal rare-earth ions in which the separation between the lowest-lying multiplet levels is large. In this case the Wigner-Eckart theorem[25] allows the substitutions

$$\vec{L} + 2\vec{S} \rightarrow g\vec{J} ,$$

$$\vec{S} \rightarrow (g-1)\vec{J} ,$$

$$\vec{L} \rightarrow (2-g)\vec{J} ,$$

and Eq. (2.5) becomes

$$\mathcal{H} = V_c + \mu_B g J^z \{ H[1 + 2J(0)\rho(g-1)/g] + \lambda m^i \} , \tag{2.8}$$

where it is useful to define a molecular-field parameter λ by

$$\lambda = \frac{2}{\mu_B^2} \left(\frac{g-1}{g} \right)^2 \mathcal{J}_{ff} . \tag{2.9}$$

We now assume that the crystal-field-only Hamiltonian

$$\mathcal{H}_c = V_c + \mu_B g J^z H \tag{2.10}$$

has been solved to give the crystal field susceptibility $\chi_c(T)$, where

$$m^i = \chi_c(T) H . \tag{2.11}$$

It follows that when Eq. (2.8) is to be solved

$$m^i = \chi_c(T) \{ H[1 + 2J(0)\rho(g-1)/g] + \lambda m^i \} ; \tag{2.12}$$

therefore,

$$m^i [1 - \lambda \chi_c(T)] = \chi_c(T) H [1 + 2J(0)\rho(g-1)/g] . \tag{2.13}$$

Now from Eq. (2.7),

$$m^e = 2J(0)\rho\left(\frac{g-1}{g} \right) m^i , \tag{2.14}$$

so that

$$(m^i + m^e)[1 - \lambda \chi_c(T)] = \chi_c(T)[1 + 2J(0)\rho(g-1)/g]^2 H . \tag{2.15}$$

If the "dressed" susceptibility of the ions is defined by

$$\chi(T) = (m^i + m^e)/H , \tag{2.16}$$

then the following equation is obtained:

$$\chi^{-1}(T)[1 + 2J(0)\rho(g-1)/g]^2 = \chi_c^{-1}(T) - \lambda \tag{2.17}$$

or

$$\chi_T(T) = \frac{\chi_c(T)[1 + 2J(0)\rho(g-1)/g]^2}{1 - \lambda \chi_c(T)} + \chi_M , \tag{2.18}$$

where $\chi_T(T)$ is the total susceptibility of the metal and χ_M is the matrix susceptibility per magnetic atom. Equation (2.17) reduces to the the one derived by Bleaney[18] in the case where $J(0)\rho = 0$, and Bleaney's criterion for the occurrence of ferromagnetic ordering at a temperature T_c $[\lambda\chi_c(T_c) = 1]$ is seen to remain valid for a metal. For a material of point symmetry lower than cubic, the parameters in Eq. (2.18) will in general be anisotropic and there will be a separate equation of the type (2.18) for each principal axis of the susceptibility tensor.

It can be seen from Eq. (2.17) that the effect of the part of the s-f interaction which is not associated with the Heisenberg couplings between the ions is merely to multiply the ionic susceptibility which the material would have without it by a factor of $[1 + 2J(0)\rho(g-1)/g]^2$. This part of the s-f interaction, as manifested in Eq. (2.17), does not appear to be able by itself to induce spontaneous ordering of an ion whose crystal field ground state is nonmagnetic, as has been suggested by Mahanti and Varma.[26] It is possible that the difference between Eq. (2.17) and the expression of Mahanti and Varma arises because they based their theory on a treatment of the s-f interaction, whose relation to Yosida's effective Hamiltonian is not entirely straightforward to see.

In obtaining the effective Hamiltonian which was used as the starting point for the susceptibility calculation, the $n = m$ term of the Heisenberg-interaction Hamiltonian $-\sum A_{n,m} \vec{S}_n \cdot \vec{S}_m$ was omitted. This means that to the Hamiltonian of each ion a term $\mathcal{H}_s$, which describes the self-energy of the ion in its own spin polarization cloud, should be added where

$$\mathcal{H}_s = -A_{nn} \vec{S}^2 . \tag{2.19}$$

Now the states of a rare-earth ion are to a good approximation described by the Russell-Saunders coupling scheme and can be written in a conventional form $|LSJM\rangle$. Then because $\vec{S}^2 |LSJM\rangle = S(S+1)|LSJM\rangle$, the only effect of H_s is to lower each state in energy by $A_{nn}S(S+1)$. $\mathcal{H}_s$ cannot mix Russell-Saunders coupled states, and in particular it cannot mix higher-lying crystal field states into a nonmagnetic ground state and so spontaneously polarize a non-Kramers ion; therefore $\mathcal{H}_s$ need not be taken account of when considering rare-earth materials.

As well as the susceptibility, it is also straightforward to calculate the quantity $\langle S^z \rangle_T / H$, which is of interest because it is proportional to the excess Knight shift. $\langle S^z \rangle_T$ is related to m^i by

$$\frac{\langle S^z \rangle_T}{H} = \frac{(g-1)\langle J^z \rangle_T}{H} = -\frac{1}{\mu_B} \left(\frac{g-1}{g} \right) \frac{m^i}{H} \tag{2.20}$$

by the Wigner-Eckart theorem, and from Eqs. (2.13) and (2.20), we obtain

$$\frac{\langle S^z\rangle}{H} = -\frac{1}{\mu_B}\left(\frac{g-1}{g}\right)\chi(T) \times\left(1+\frac{2J(0)\rho(g-1)}{g}\right)^{-1}, \qquad (2.21)$$

and we see that the excess Knight shift is exactly proportional to the "dressed" ionic susceptibility providing that ρ does not vary with temperature.

Such variations of the matrix susceptibility can have significant effects upon the total susceptibility, not so much through their influence upon the term $J(0)\rho$, which will give only a second-order effect, but through their influence on the molecular-field parameter λ. Kasuya[1] has used this idea to explain why the proportional increases of the effective paramagnetic moments of the heavy rare-earth metals are so much smaller than the increases of the effective ferromagnetic moments, which from Eq. (2.14) are given by $[1+2J(0)\rho \times(g-1)/g]$. For example, for gadolinium (the data are taken from Kasuya's review) the effective ferromagnetic moment is $7.55\mu_B$, which is 8% greater than the free-ion value, while the paramagnetic moment is only 0.5% greater. (However, in comparing the paramagnetic moment to the ferromagnetic moment it should be remembered that the latter results from an electron gas which is strongly magnetized to a value of $0.55\mu_B$ per atom, and so the linear-response approximation, which we have implicitly been using in this paper, may not be too good.) It is worthwhile to review Kasuya's argument, as we shall need it when examining the susceptibilities of the light rare-earth metals in Sec. III.

It has been established by Penney and Schlapp[27] that crystal fields may have the effect of converting the susceptibility of a free rare-earth ion, which is of the form C/T, into the form $\chi_c(T) = C'/(T-\Omega)$ for a polycrystalline specimen over a range of several hundred degrees kelvin, where Ω is negative and C' is slightly greater than C, provided that the temperature of measurement is not too low compared with the crystal-field splittings. For instance, in the calculations which Williams and Hirst[11] made of the susceptibilities of heavy rare-earth ions subjected to a cubic-crystal field, it was found that although the overall crystal-field splittings were in the region of 100–200 °K, susceptibility behavior of the form $C'/(T-\Omega)$ persisted down to 10–40 °K, and that $-\Omega$ was of the order of 2–10 °K. However $-\Omega$ can be substantially larger than this; for example, in $Yb_2(SO_4)_3 \cdot 8\,H_2O$ it is +42 °K.[28]

Therefore, in the temperature regime in which the expression $\chi_c(T) = C'/(T-\Omega)$ is valid,

$$\chi^{-1}(T) = [T-\Omega-C'\lambda(T)]/C'[1+2J(0)\rho(g-1)/g]^2 \qquad (2.22)$$

from Eq. (2.17), and hence

$$\frac{\partial}{\partial T}[\chi^{-1}(T)] = \frac{1-C'(\partial/\partial T)\lambda(T)}{C'[1+2J(0)\rho(g-1)/g]^2} \qquad (2.23)$$

Now it is reasonable to assume that the molecular-field parameter λ [Eq. (2.9)], which depends upon the wave-vector-dependent susceptibility of the conconduction-electron system, has the temperature dependence

$$\lambda(T) = \lambda_0(1-T^2/T_F^2), \qquad (2.24)$$

where T_F is of the order of the degeneracy temperature of the electron gas, although at temperatures above room temperature a linear dependence on temperature seems to be more satisfactory for the heavy rare-earth metals.[1] Therefore,

$$\left(\frac{\partial}{\partial T}\chi^{-1}(T)\right)^{-1} = \frac{C'[1+2J(0)\rho(g-1)/g]^2}{1+2TT_\theta/T_F^2}, \qquad (2.25)$$

where $T_\theta = \lambda_0 C'$, and so the ratio of the effective paramagnetic moment p, which is deduced from the slope of the inverse susceptibility curve at a temperature T, to the bare moment $p_0 = g[J(J+1)]^{1/2}$ is

$$p/p_0 = [1+2J(0)\rho(g-1)/g](1-TT_\theta/T_F^2). \qquad (2.26)$$

In obtaining this equation from the one above we have assumed that the value of C' is very close to that of C. We shall see in Sec. III that this assumption leads to some very reasonable results, but nevertheless it can only be rigorously justified by an accurate crystal field calculation. The assumption will, however, be a good one for gadolinium materials as these have crystal-field splittings which are very small.

From the value of the effective ferromagnetic moment of gadolinium metal, it may be deduced that $J(0)\rho = +0.08$, and from the value of the effective paramagnetic moment, measured at, say, $T = 600$ °K and taking $T_\theta = 300$ °K, it may be deduced from Eq. (2.26) that T_F is in the region of 1600 °K. Usually in metallic rare-earth materials $TT_\theta/T_F^2 \ll 1$ and the effective paramagnetic moment is temperature independent; only for the heavy rare-earth metals is the second factor large enough to need to be taken account of. In his original derivation Kasuya[1] assumed a linear dependence of λ upon temperature. This results in an effective moment which is modified by a numerical factor but which is also temperature independent, in agreement with the experimental results for most of the heavy rare-earth metals. However, it is important to note that the quadratic temperature dependence of Eq. (2.24) can in principle provide a mechanism for deviations from linearity of a plot of $\chi^{-1}(T)$ against temperature in the high-temperature paramagnetic regime.

C. Susceptibility of Metals Containing Samarium

In the discussion of the susceptibility of metallic samarium compounds which is given in this section, the following assumptions are made: First, the Heisenberg exchange interactions between the magnetic ions are treated in the molecular-field approximation; second, crystal field effects are neglected; third, it is assumed that only the lowest angular momentum level of the ion is thermally populated: No further physical or mathematical approximations enter the theory thereafter. This means that the theory is applicable only in the temperature range in which the latter two restrictions do not make themselves felt. For the particular samarium materials whose susceptibility data are analyzed in Sec. III, this range appears to be from 15 to about 230 °K, but for other materials it may be different. It is straightforward to generalize the theory to take account of the thermal population of higher-lying J levels in the manner of De Wijn *et al.*,[16] and this will be the subject of a future paper.

The single-ion Hamiltonian of the problem is therefore

$$\mathcal{H}=\mu_B(L^z+2S^z)H+\mu_B 2S^z[J(0)\rho H-\langle S^z\rangle_T\mathcal{J}_{ff}/\mu_B], \tag{2.27}$$

which may be written

$$\mathcal{H}=\mu_B(L^z+2S^z)H+\mu_B 2S^z H_e\ , \tag{2.28}$$

where H_e, the total exchange field, is given by

$$H_e=J(0)\rho H-\langle S^z\rangle_T\mathcal{J}_{ff}/\mu_B\ . \tag{2.29}$$

It is known[9] that a Hamiltonian of the form $\mu_B(L^z+2S^z)H$ gives rise to a susceptibility per ion $\chi_i=-\mu_B\langle L^z+2S^z\rangle_T/H$ obtained from

$$-\langle L^z+2S^z\rangle_T/H=a/T+b\ , \tag{2.30}$$

where

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

$$b=\frac{\mu_B F(J+1)}{6(2J+1)\Delta}\ , \tag{2.31}$$

$$F(J)=[(S+L+1)^2-J^2][J^2-(S-L)^2]/J\ , \tag{2.32}$$

and where g and J refer to the lowest J level and Δ is the energy separation between that and the $(J+1)$ level. For the lowest multiplet level of the tripositive samarium ion $J=\frac{5}{2}$, and putting the values of the quantum numbers S and L into Eq. (2.32), it is found that $b=20\mu_B/7\Delta$.

White and Van Vleck[20] have shown that when an exchange field is present as well, as in Eq. (2.28), then the following expressions are valid:

$$-\langle L^z+2S^z\rangle_T=a[H+2H_e(g-1)/g]/T+b(H+2H_e)\ , \tag{2.33}$$

$$-\langle S^z\rangle_T=a[H+2H_e(g-1)/g](g-1)/gT+b(H+2H_e)\ . \tag{2.34}$$

The equations may be obtained by treating the Hamiltonian of Eq. (2.28) by perturbation theory and calculating the thermal averages of the operators S^z and (L^z+2S^z). They may also be obtained by the more concise but equally rigorous arguments of White and Van Vleck. The essential point which they use is that the matrix elements of the operators $\vec{S}$ and $(\vec{L}+2\vec{S})$ between states of different J are exactly the same, because the operator $\vec{J}=(\vec{L}+\vec{S})$ is by definition diagonal in the quantum number J.

The procedure for solving Eqs. (2.29), (2.33), and (2.34) is first to substitute (2.29) into (2.34) in order to get a self-consistent value for $\langle S^z\rangle_T/H$. Having obtained this, the extra conduction-electron magnetization m^e may be got from Eq. (2.7) and the exchange field H_e from Eq. (2.29). The latter may then be substituted into Eq. (2.33) and so $\langle L^z+2S^z\rangle_T/H$ and hence the ionic magnetization m^i [Eq. 2.6] are obtained. To this is added the conduction-electron magnetization m^e, and the sum of the two divided by H gives the "dressed" susceptibility per ion. Some of the algebraic steps in this calculation are given in more detail in the Appendix.

First we substitute (2.29) into (2.34) to obtain

$$-\langle S^z\rangle_T/H=\frac{T_\infty}{T_\theta}\times\frac{b\{T[1+2J(0)\rho]-T_0[1+2J(0)\rho(g-1)/g]\}}{(T-T_\infty)}\ , \tag{2.35}$$

where it has been found useful to combine some of the parameters into the forms

$$T_0=-\left(\frac{g-1}{g}\right)\frac{a}{b}\ , \tag{2.36a}$$

$$T_\theta=\frac{2\mathcal{J}_{ff}a}{\mu_B}\left(\frac{g-1}{g}\right)^2, \tag{2.36b}$$

$$\frac{T_\infty}{T_\theta}=1-\left(\frac{g}{g-1}\right)\frac{T_\infty}{T_0}$$

or

$$\frac{T_\theta}{T_\infty}=1+\left(\frac{g}{g-1}\right)\frac{T_\theta}{T_0}\ , \tag{2.36c}$$

the latter two equations being equivalent. In the limit of an infinitely large multiplet separation Δ, b approaches zero and Eq. (2.35) becomes

$$-\langle S^z\rangle_T/H=\left(\frac{g-1}{g}\right)\frac{a[1+2J(0)\rho(g-1)/g]}{(T-T_\theta)}\ , \tag{2.37}$$

and it is seen that T_θ is the paramagnetic Curie temperature which the system would possess if Van Vleck transitions were absent.

From Eq. (2.36c) it is apparent that if the condition $gT_\theta/(g-1)\,T_0=-1$ is obeyed, then T_∞ will approach infinity and $\langle S^z\rangle_T/H$ will be divergent at finite temperatures, as will the total susceptibility, because we shall see later that this contains a term which also has a denominator of the form $(T-T_\infty)$. In this situation there will, therefore, be a polarization catastrophe, somewhat analogous to that discussed by Trammell[29] and Bleaney[18] for a rare-earth ion with a nonmagnetic crystal field ground state, but in our case it is the $J=\frac{7}{2}$ multiplet level which will be spontaneously mixed into the ground-state $J=\frac{5}{2}$ level by the exchange field.

Van Vleck[9] has found that a screening factor σ of 33 accounts best for the susceptibility of samarium salts, and from this value a splitting of 1550 °K between the $J=\frac{5}{2}$ and $J=\frac{7}{2}$ multiplet levels may be calculated. Using Eqs. (2.31) and (2.32) the value $T_0=322$ °K is obtained. As $g=\frac{2}{7}$ for the samarium $J=\frac{5}{2}$ level, it is found from Eq. (2.36c) that T_θ must be greater than 800 °K for the polarization catastrophe to occur. This value is rather large, and the phenomenom does not yet seem to have been observed in compounds whose only magnetic constituent is samarium.

Equation (2.35) shows that the temperature T_{k0} at which the excess Knight shift changes sign is given by

$$T_{k0}=T_0\,[1+2J(0)\rho(g-1)/g]/[1+2J(0)\rho]\,. \tag{2.38}$$

and not $T_{k0}=T_0$, as given by the theory of White and Van Vleck.[20] Using the value $J(0)\rho=+0.1$, which as we shall see in Sec. III may be suitable for samarium metal, a value of roughly 150 °K is obtained for T_{k0} in contrast with 322 °K if $J(0)\rho$ is zero. This effect is however probably not adequate to explain the nonobservance of a Knight-shift crossover in the compound $\mathrm{SmAl_2}$.[21] The value of $J(0)\rho$ deduced from the paramagnetic moment of the isostructural compound $\mathrm{GdAl_2}$[30] is very small indeed, and it is likely that the crystal field effects discussed by Malik and Vijayaraghavan[10] are needed to provide the explanation.

We now return to the calculation of the susceptibility. From Eqs. (2.7) and (2.35) we obtain an expression for the conduction-electron magnetization m^e associated with each ion,

$$\begin{aligned} m^e/\mu_B H = -\,2J(0)\rho\left(\frac{g-1}{g}-\frac{T_\infty}{T_0}\right)\frac{a}{(T-T_\infty)} \\ \times\{\,[1+2J(0)\rho]\;T/T_0-[1+2J(0)\rho(g-1)/g]\}\,, \end{aligned} \tag{2.39}$$

and from Eqs. (2.29) and (2.35) an expression for the exchange field H_e:

$$\begin{aligned} 2H_e/H = 2J(0)\rho-\frac{T_\infty}{T_0(T-T_\infty)}\,\frac{g}{(g-1)} \\ \times\{\,T\,[1+2J(0)\rho]-T_0[1+2J(0)\rho(g-1)/g]\}\,. \end{aligned} \tag{2.40}$$

We may now substitute the above equation into Eq. (2.33) to obtain

$$\begin{aligned} -\,\langle L^z+2S^z\rangle_T/H = b\,[1-gT_\infty/(g-1)\,T_0] \\ +\frac{a}{(T-T_\infty)}\,\{(1-T_\infty/T_0)^2+(1-T/T_0) \\ \times[(g-1)/g-T_\infty/T_0]\,2J(0)\rho\}\,. \end{aligned} \tag{2.41}$$

Now $m^e/\mu_B H$ may be added to this to obtain the final result, $\chi(T)/\mu_B=(m^e+m^i)/\mu_B H$:

$$\begin{aligned} \chi(T)/\mu_B = b\,[1-g\,T_\infty/(g-1)\,T_0][1+2J(0)\rho]^2 \\ +\frac{a}{(T-T_\infty)}\{1+2J(0)\rho(g-1)/g-[1+2J(0)\rho]\,T_\infty/T_0\}^2\,. \end{aligned} \tag{2.42}$$

An interesting feature of this equation is that the temperature dependence only enters through the term in the denominator; a Curie-Weiss type of behavior occurs. For the free ion

$$\chi(T)/\mu_B=b+a/T \tag{2.43}$$

and for an ion subjected to the exchange couplings and conduction-electron polarization effects which we have analyzed here,

$$\chi(T)/\mu_B=b^*+a^*/(T-T_\infty)\,, \tag{2.44}$$

where a^* and b^* are defined by Eq. (2.42). Of course, to obtain the total susceptibility of the metal, the matrix contribution χ_M/μ_B must be added onto Eqs. (2.42) and (2.44).

III. COMPARISON WITH EXPERIMENT

A. Samarium

Measurements of the susceptibility of samarium metal have been made by Lock,[31] Schieber *et al.*,[32] and Jayaraman and Sherwood.[33] The latter made measurements up to room temperature on polycrystalline specimens of both the rhombohedral form of samarium and also of the double-hexagonal-close-packed (dhcp) structural modification, which can be formed at moderate temperatures and pressures. We shall now compare the theory of Sec. II C with their results.

In their paper Jayaraman and Sherwood plotted the magnetization of the metals at a field of 15 300 Oe. However, as Schieber *et al.*[32] have reported that the magnetization-field curves are linear up to 16 800 Oe, the magnetization readings[34] have been converted into susceptibility ones by dividing by 15 300, and these are plotted as the points in Figs. 1 and 2.

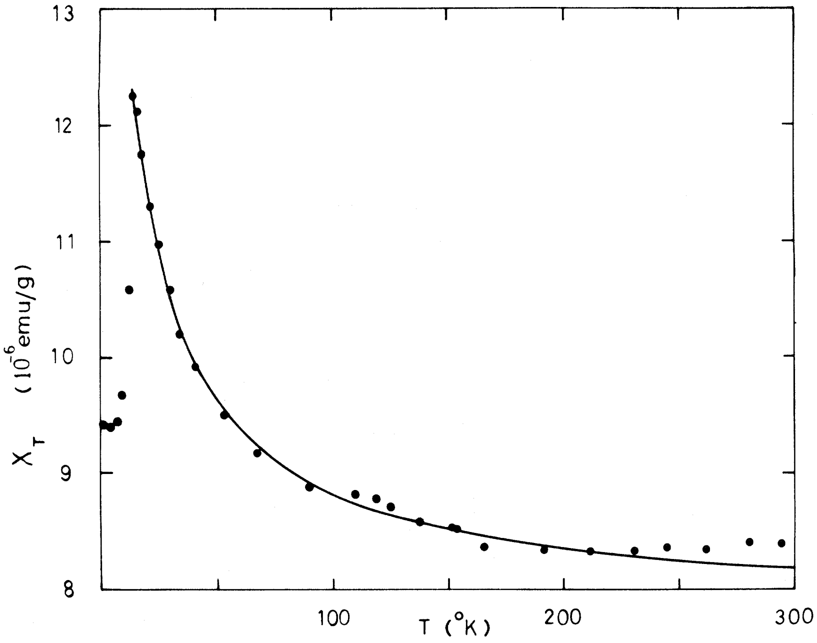

FIG. 1. Magnetic susceptibility of rhombohedral samarium metal plotted against temperature. The data points are obtained from Ref. 33, and the continuous curve obeys the equation $\chi_T(T) = [7.838 + 106.781/(T + 9.458)] \times 10^{-6}$.

Equation (2.42) predicts that the total susceptibility of the metal will be of a quasi-Curie-Weiss form,

$$\chi_T(T) = \chi_0 + D/(T - \theta) , \tag{3.1}$$

and the continuous lines in Figs. 1 and 2 indicate the best least-squares fits of an expression of this nature to the experimental points of Jayaraman and Sherwood. We first discuss the data for rhombohedral samarium shown in Fig. 1.

For this material, only the experimental points in the range 15–231 °K were used for the computer fit. The parameters which gave the best fit to Eq. (3.1) were $D = 106.78 \times 10^{-6}$, $\chi_0 = 7.838 \times 10^{-6}$, and $\theta = -9.458$. Now the susceptibility of samarium metal, if it were considered to be an assembly of noninteracting free ions with only the $J = \frac{5}{2}$ multiplet level thermally populated, would be given by Van Vleck's theory as [Eq. (2.43)]

$$\chi(T) = (594/T + 4.61) \times 10^{-6} \text{ emu/g} , \tag{3.2}$$

using Eqs. (2.31) and (2.32) and taking the number of atoms per gram to be 40.1×10^{20}. This allows the quantities a and b to be obtained and hence the quantities $J(0)\rho$ and T_θ to be deduced from Eqs. (2.42) and (2.36).

The parameter $D = 106.78 \times 10^{-6}$, which we define as the "effective Curie constant" of the samarium ion in rhombohedral samarium metal,

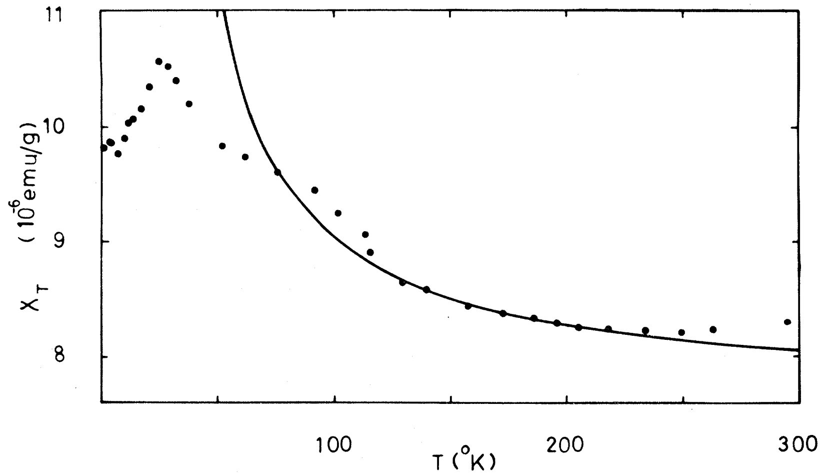

FIG. 2. Magnetic susceptibility of dhcp samarium metal plotted against temperature. The data points are obtained from Ref. 33, and the continuous curve obeys the equation $\chi_T(T) = [7.681 + 105.329/(T - 21.115)] \times 10^{-6}$.

is 594/106.78 = 5.57 times smaller than that of the free ion. From Eq. (2.42) we obtain

$$(5.57)^{-1/2} = 1 + 2J(0)\rho(g-1)/g - (1+2J(0)\rho)\,T_\infty/T_0 \,. \quad (3.3)$$

T_0 is taken to be 322 °K and T_∞ is identified from Eqs. (2.42) and (3.1) as -9.458 °K. Using these numbers the value $J(0)\rho = +0.123$ is obtained from Eq. (3.3). The value of $J(0)\rho$ estimated from the saturation magnetization of gadolinium is + 0.08, as mentioned in Sec. II B, so the value obtained for rhombohedral samarium is not too unreasonable. It is seen then that conduction-electron polarization effects which *enhance* the moment of gadolinium *reduce* the moment of samarium, although in the latter case the proportional change in moment is much greater, mainly because for samarium $(g-1)/g$ is five times larger in magnitude than for gadolinium. From Eq. (2.36c) T_θ, which Eq. (2.36b) shows to be a direct measure of $\mathcal{J}_{ff}$, is calculated to be -9.6 °K; a net antiferromagnetic exchange interaction is therefore indicated, and this is borne out by the observation of a Néel point at about 15 °K.

Since we now know $J(0)\rho$ and T_∞, the theoretical value of the temperature-independent contribution to the susceptibility may be calculated from Eq. (2.42) to be 1.532 b. Because b corresponds to 4.61×10^{-6} emu/g [Eq. (3.2)] this contribution comes to 7.06×10^{-6} emu/g. Now the parameter $\chi_0 = 7.84\times10^{-6}$ emu/g, which was obtained from the computer fit, contains the matrix susceptibility as well as this contribution. The theory therefore predicts the matrix susceptibility to be equal to $(7.84-7.06)\times10^{-6} = +0.78\times10^{-6}$ emu/g. The susceptibility of lanthanum, a material which might be expected to have matrix properties fairly similar to those of samarium, has been measured by Lock [31] to be 0.75×10^{-6} emu/g at room temperature and rather greater at lower temperatures. The agreement between the two values seems satisfactory.

The theoretical curve fits the experimental points in Fig. 1 to an accuracy of 1% between 15 and 230 °K, but it can be seen that there are deviations from it at both low and high temperatures. At about 15 °K magnetic ordering occurs and the theory becomes invalid. However, what is surprising is that the theory fits so very well down to 15 °K, in spite of the fact that crystal field effects are known to often give rise to marked deviations from linearity of $\chi^{-1}(T)$-vs-T plots for normal rare-earth ions below about 50 °K. Measurements of the susceptibility of polycrystalline specimens would tend to mask deviations caused by crystal fields, which might be more apparent in single-crystal specimens. It is possible also that crystal-field splittings in this material may happen to have little effect upon the susceptibility or be very small. The situation is not yet clear.

Above 230 °K there are also deviations from the theoretical expression. The following rough calculation shows that these are due to the thermal occupation of higher multiplet levels.

We assume that the extra contribution to the susceptibility arises entirely from the population of the $J=\frac{7}{2}$ level, which lies $\Delta = 1550$ °K above the $J=\frac{5}{2}$ ground state, and that the susceptibility contributed by this higher level consists only of the Curie term relevant to it. Since the effective moment $g[J(J+1)]^{1/2}$ of the $J=\frac{7}{2}$ level is $3.28\mu_B$ and is far greater than that of the $J=\frac{5}{2}$ level, which is 0.845 μ_B, it follows that the susceptibility arising from Van Vleck transitions from the $J=\frac{7}{2}$ level will tend to be smaller, relative to the Curie term, than for the $J=\frac{5}{2}$ level at the same temperature. Heisenberg exchange couplings will also tend to be small for the $J=\frac{7}{2}$ level, because its spin projection $(g-1)^2J(J+1)$ is only 0.48, compared to the 4.46 of the similar quantity for the $J=\frac{5}{2}$ level.

Therefore it is reasonable to estimate the contribution of the $J=\frac{7}{2}$ level to the susceptibility as being of the form

$$[\hat{N}\mu_B^2(3.28)^2/3kT]\,e^{-\Delta/T}\,, \quad (3.4)$$

where $\hat{N}$ is the number of samarium atoms per gram. At a temperature of 300 °K the susceptibility contribution of Eq. (3.4) comes to about 0.2×10^{-6} emu/g, in good agreement with the difference between the experimental points and the theoretical curves in Figs. 1 and 2. This difference, and also the feature that the susceptibility of samarium rises again after a minimum at about 230 °K, are therefore attributed to the thermal population of higher multiplet levels. The reason why the minimum is observed at such a low temperature as 230 °K, in contrast to the 450 °K obtained in the calculation for insulators which was discussed by Van Vleck, [9] is that the large antiparallel conduction-electron polarization clothing of the $J=\frac{5}{2}$ level of the ion has substantially reduced its moment from the free-ion value, whereas the moment of the $J=\frac{7}{2}$ level is little altered because its value of $(g-1)/g$ is rather small $(-\frac{11}{52})$.

A small anomaly in the susceptiblity can be seen at about 110 °K. Measurements of the resistivity[35] and heat capacity[36] of polycrystalline specimens of nominally rhombohedral samarium have indicated that there may be a magnetic transition at this temperature. However, the observation of a distinct transition, also at 110 °K in dhcp samarium, which can be seen in Fig. 2, raises the possibility that the specimens of rhombohedral samarium may have contained small quantities of the dhcp structural modification. If, however, further experimental work confirms that the 110 °K transition is indeed intrinsic to rhombohedral samarium, then it will be necessary to reinterpret the temperature dependence between 15 and 110 °K of the susceptibility data in Fig. 1 in some other manner. Possibly it may arise from one unordered sublattice while another, which has ordered at 110 °K, gives a temperature-independent contribution to the susceptibility.

The magnetic behavior of dhcp samarium is seen in Fig. 2 to be rather more complicated than that of rhombohedral samarium. There are susceptibility anomalies at 15, 27, and 110 °K whose origins are at present unknown. In fitting the data to Eq. (3.1) we have used only the experimental points between 130 and 210 °K. The parameters obtained from the fit are $\chi_0 = 7.681\times10^{-6}$ emu/g, $D = 105.329\times10^{-6}$ emu/g, and $\theta = 21.115$ °K. Although the temperature range over which the fit has been made is rather narrow, the experimental points obey Eq. (3.1) well, as may be seen from Fig. 3 in which $[\chi_T(T) - 7.681\times10^{-6}]^{-1}$ is plotted against T, where $\chi_T(T)$ are the experimental values of the susceptibility. The ordinate of the straight line is given by $(T - 21.115)/(105.329\times10^{-6})$, which is the best least-squares fit to these points.

The parameters were analyzed in exactly the same manner as were those of rhombohedral samarium, and the following results were obtained. The effective moment of the samarium ion in dhcp samarium is 2.37 times smaller than the free-ion value, $J(0)\rho = +0.10$, $T_\theta = +20.6$ °K, and the temperature-independent contribution to the ionic susceptibility, which appears in Eq. (2.42), is $1.475b$. Taking b to correspond to 4.61×10^{-6} emu/g, an ionic temperature-independent contribution to the susceptibility of 6.80×10^{-6} emu/g is obtained. Since $\chi_0 = 7.681\times10^{-6}$ emu/g, it follows that the matrix susceptibility of dhcp samarium is 0.88×10^{-6} emu/g, which again is in reasonable agreement with the value for lanthanum[31] of 0.75×10^{-6} emu/g. We conclude that the susceptibility of dhcp samarium agrees well with the theory of Sec. II C in the temperature region in which it is valid.

B. Light Rare Earths

Accurate measurements of the susceptibilities of single crystals of europium, neodymium, and praeseodymium have recently been made by Johansson *et al.*,[37] and from their results for the effective paramagnetic moments of these materials some information about the quantity $J(0)\rho$ may be extracted. It is important to note that while the paramagnetic moments of the heavy rare earths could not give unambiguous information about $J(0)\rho$, as the temperature dependence of the molecular-field parameter gave an extra contribution to the slope of the inverse susceptibility curve [Eq. (2.26)], this is not the case for the light rare earths. Because their ordering temperatures are low, and because the temperatures at which the slopes of their inverse susceptibility curves may be estimated are also low compared to the similar quantities for the heavy rare earths, the fractional change of the effective paramagnetic moments of the light rare-earth metals is given by $1 + 2J(0)\rho(g-1)/g$ within the limitations of the model of Sec. II B.

Johansson *et al.*[37] found the paramagnetic moment of europium metal (this material is exceptional in that the europium ion is divalent and in $4f^7$ configuration) to have the value $8.48\mu_B$ compared with the $7.94\mu_B$ of the free ion. This leads to a value of $J(0)\rho = +0.07$.

The effective moments of neodymium and praeseodymium, as deduced from their inverse susceptibility curves, were found to be anisotropic. To obtain an estimate of an average $J(0)\rho$, we have taken the polycrystalline moment to be the sum of one-third of the moment for the c direction plus two-thirds of the moment for the basal plane. In this way we obtain 3.50 and $3.43\mu_B$ for praeseodymium and neodymium and hence $J(0)\rho = +0.05$ and $+0.08$, respectively.

However Lock,[31] who made an earlier measurement of the susceptibility of polycrystalline neodymium, found that its susceptibility could be best represented by the equation

$$\chi_T(T) = D/(T - 4.3) + 5.0\times10^{-6}\ \text{emu/g}, \qquad (3.5)$$

where D corresponds to a paramagnetic moment of $3.3\mu_B$, as compared to the $3.62\mu_B$ of the free ion. A part of the temperature-independent component of the susceptibility is expected to come from Van Vleck transitions between the ground $J = \frac{9}{2}$ level and the $J = \frac{11}{2}$ level, which lies about 3000 °K above it. If the theory of Sec. II C is used to analyze Lock's data in exactly the same way as it has been used on the samarium data in Sec. III A, the result is obtained that $J(0)\rho = +0.12$, and that the temperature-independent contribution to the ionic susceptibility in Eq. (2.42) should be 1.75×10^{-6} emu/g. If we add to this the susceptibility of lanthanum, which has been found in Sec. III A to correspond fairly well to the matrix susceptibility of samarium, we obtain the result that the total temperature-independent component of the susceptibility of neodymium should be about 2.5×10^{-6} emu/g, rather than the value obtained by Lock,[31] which is twice this size. It is to be hoped that future high-temperature measurements of the susceptibility of neodymium will clarify the reasons for this discrepancy.

Finally we come to the estimation of $J(0)$ from the quantity $J(0)\rho$. It is recognized from linear-response-theory arguments[19] that ρ is directly

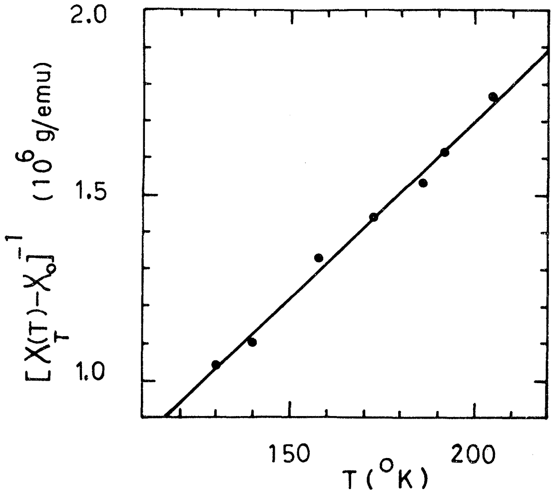

FIG. 3. Susceptibility data for dhcp samarium metal plotted against temperature. The points are given by $[\chi_T(T) - 7.681\times10^{-6}]^{-1}$, where $\chi_T(T)$ are the data points of Ref. 33, and the ordinate of the straight line is given by $(T - 21.115)/(105.329\times10^{-6})$.

proportional to the uniform Pauli spin susceptibility of the matrix. If we use the value of the susceptibility of lanthanum metal, ρ is calculated from Eq. (1.4) to be 1.61 states/eV atom. However this is likely to be an underestimate, because in putting the measured susceptibility of lanthanum into Eq. (1.4), we have included the diamagnetic contributions. The quantity ρ for europium metal has arbitrarily been taken to have a value smaller by a factor of $(\frac{2}{3})^{1/2}$, as it contains only two conduction electrons per atom, as compared to the three of the other rare earths. In Table I we show the estimated values of $J(0)\rho$ and $J(0)$ for those rare-earth metals which have been mentioned in this paper. The values of $J(0)$ in the table may be compared with a value of + 0.0365 eV obtained from the energy difference between the ^7S and ^9S spectroscopic states of the free dipositive gadolinium ion, which is caused by the exchange interaction between the electrons in the 6s and 4f shells.[38] The agreement in magnitude is good, and the agreement in sign strongly suggests that the s-f interaction mechanism in these light rare earths is due to s-f exchange and not to s-f mixing, as is clearly the case in many cerium materials.[39]

If, however, the susceptibility of lutetium were used to calculate ρ, this quantity would be about five times smaller and the values of $J(0)$ would be correspondingly higher. It appears, then, that the metallic matrices of the rare-earth metals in the first half of the series have properties which are more similar to those of lanthanum than to lutetium.

IV. CONCLUSIONS

The purpose of this paper has been to elucidate the effects which conduction-electron polarization has upon the paramagnetic properties of rare-earth materials. An expression has been obtained for the susceptibility of a metallic material which contains normal rare earths, which takes account of the effects of the crystal field, of conduction-electron polarization, and of Heisenberg exchange interactions between the rare-earth ions treated in a molecular-field approximation. It has been emphasized, although this suggestion is hardly new, that accurate measurements of the effective paramagnetic moments of rare earths in metallic materials give valuable information about the magnitude of the s-f coupling constant $J(0)$, and also information about the *sign* of $J(0)$, which is difficult to obtain by other means, but fundamentally very important.

An expression for the paramagnetic susceptibility of metallic samarium materials has been derived which takes account of the Van Vleck transitions between multiplet levels induced by both the applied magnetic field and the exchange fields, and of the induced conduction-electron polarization. Crystal-field splittings are neglected and the assumptions are made that the samarium ions are in a well-defined $4f^5$ configuration and that only the lowest multiplet level is thermally populated. However, despite these shortcomings, the theory is found to fit the experimental values of the susceptibility of dhcp samarium over the temperature range 110–230 °K and the susceptibility of rhombohedral samarium over a wider range, although in the latter case there is at present some ambiguity in the interpretation of the data. The parameters obtained from the fits compare well with those obtained for the other light rare-earth metals. It is found that the key feature of the theory which allows it to describe the experimental results so

TABLE I. Estimated values of the s-f coupling constant $J(0)$ and of $J(0)\rho$ for some of the rare-earth metals in the first half of the series. See the text for discussions of the calculation of ρ and of the validity of the rhombohedral samarium data. The values of $J(0)$ may be compared with the $4f$–$6s$ exchange integral of +0.0365 eV obtained from the spectroscopic properties of the free divalent gadolinium ion.

Metal	$J(0)\rho$	$J(0)$ (eV)
Pr	+0.048	+0.030
Nd	+0.076	+0.047
Sm(Rh)	+0.123	+0.076
Sm(dhcp)	+0.100	+0.062
Eu	+0.070	+0.049
Gd	+0.080	+0.050

well is the incorporation of conduction-electron polarization effects, which are far greater for samarium than for the other rare earths. In fact, this causes what might be called the effective Curie constant of the samarium ion in samarium metal to be more than five times smaller than the value expected for the free ion.

It is customary to refer to a magnetic ion which, when dissolved in a metal, has associated with it a total magnetic moment which is much greater than that on the ion itself as a giant moment. For example, Doniach and Wohlfarth[19] have commented that of the $10\mu_B$ of the archetypal giant moment *Pd*Fe, only about $3\mu_B$ actually reside at the iron site. There is as yet no consensus of opinion as to how much a moment has to be enhanced to deserve the name giant, but perhaps by a factor of 2 would be sufficient. In the same way we might call a moment which is diminished by a factor of 2 a dwarf moment.[40] By this criterion a samarium ion in rhombohedral or dhcp samarium metal bears a dwarf moment.[41,42] Severely reduced moments are of course common in Kondo[8] systems, but in this case the diminution originates from large s-d mixing rather than from the direct exchange interaction between the ionic spin and the conduction electrons as in samarium.

Finally, we have compared the values of the s-f coupling constant $J(0)$ obtained for samarium with those of some of the other light rare-earth metals and have found them to be in good agreement with the value deduced from spectroscopic data.

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APPENDIX

In this Appendix the algebraic steps required in going from Eq. (2.33) and (2.34) to (2.42) are indicated. We shall, for brevity, use the substitution $\gamma = 2J(0)\rho$.

If Eq. (2.29) is substituted into (2.34) we obtain

$$-\langle S^z\rangle_T\left\{1-\frac{2\mathcal{J}_{ff}}{\mu_B}\left[\left(\frac{g-1}{g}\right)^2\frac{a}{T}+b\right]\right\}\Big/H = \left(\frac{g-1}{g}\right)\frac{a}{T}\left(1+\gamma\frac{g-1}{g}\right)+b(1+\gamma)\ . \tag{A1}$$

Using Eqs. (2.36) we find that

$$1-\frac{2\mathcal{J}_{ff}}{\mu_B}\left[\left(\frac{g-1}{g}\right)^2\frac{a}{T}+b\right] = \frac{T_\theta(T-T_\infty)}{TT_\infty}\ , \tag{A2}$$

whence follow Eqs. (2.35), (2.39), and (2.40), using Eqs. (2.36).

We now substitute (2.40) into (2.33) to obtain

$$-\langle L^z+2S^z\rangle_T/H = \frac{a}{T}+b+\frac{b(T-T_0)}{T}\times\left[\gamma-\left(\frac{g}{g-1}\right)\frac{T_\infty}{T_0}\left(\frac{T(1+\gamma)-T_0[1+\gamma(g-1)/g]}{T-T_\infty}\right)\right]\ , \tag{A3}$$

using

$$b+(g-1)a/gT=(T-T_0)b/T\ . \tag{A4}$$

Therefore,

$$\frac{-\langle L^z+2S^z\rangle_T}{H} = b+\frac{a}{T}\left(\frac{T-T_0}{T_0}\right)\left[\frac{T_\infty}{T_0}\ \frac{\{T(1+\gamma)-T_0[1+\gamma(g-1)/g]\}}{(T-T_\infty)}+\frac{T_0}{(T-T_0)}-\gamma\left(\frac{g-1}{g}\right)\right]\ . \tag{A5}$$

We can now expand the terms within the large brackets as

$$\frac{\{[1+\gamma(g-1)/g]+(1+\gamma)\,TT_\infty/T_0^2-(2+\gamma)\,T_\infty/T_0-(g-1)\,\gamma T/g\,T_0\}\,TT_0}{(T-T_\infty)(T-T_0)}\ ,$$

hence

$$-\langle L^z+2S^z\rangle_T/H = b+\frac{a}{(T-T_\infty)}\left[\left(1-\frac{T_\infty}{T_0}\right)^2+\left(\frac{g-1}{g}\right)\left(1-\frac{T}{T_0}\right)\gamma+\frac{TT_\infty(1+\gamma)}{T_0^2}-\frac{(2+\gamma)T_\infty}{T_0}+\frac{2T_\infty}{T_0}-\left(\frac{T_\infty}{T_0}\right)^2\right]\ , \tag{A6}$$

and from this Eq. (2.41) is obtained. This latter equation may be manipulated into the more convenient form

$$-\langle L^z+2S^z\rangle_T/H = b\left[1-\left(\frac{g}{g-1}\right)\frac{T_\infty}{T_0}\right](1+\gamma)^2+\frac{a}{(T-T_\infty)}\left\{\left(1-\frac{T_\infty}{T_0}\right)^2+\gamma\left[\left(\frac{g-1}{g}\right)-\frac{T_\infty}{T_0}\right]\left[1+(1+\gamma)\frac{T}{T_0}-(2+\gamma)\frac{T_\infty}{T_0}\right]\right\}\ . \tag{A7}$$

Onto this we add $m^e/\mu_B H$ [Eq. (2.39)] to get

$$\chi(T)/\mu_B = (m^i + m^e)/\mu_B H$$

$$= b\left[1 - \left(\frac{g}{g-1}\right)\frac{T_\infty}{T_0}\right](1+\gamma)^2 + \frac{aC^*}{T - T_\infty}, \qquad \text{(A8)}$$

where

$$C^* = (1 - T_\infty/T_0)^2 + \gamma\left[\left(\frac{g-1}{g}\right) - \frac{T_\infty}{T_0}\right]$$

$$\times\left[2 + \gamma\left(\frac{g-1}{g}\right) - (2+\gamma)\frac{T_\infty}{T_0}\right] \qquad \text{(A9)}$$

and it can be verified that C^* is a perfect square:

$$C^* = \left[1 + \left(\frac{g-1}{g}\right)\gamma - (1+\gamma)\,\frac{T_\infty}{T_0}\right]^2, \qquad \text{(A10)}$$

thus giving Eq. (2.42).

Equation (2.35) can also be cast into a quasi-Curie-Weiss form. Specifically,

$$-\frac{\langle S^z\rangle_T}{H} = \left[1 - \left(\frac{g}{g-1}\right)\frac{T_\infty}{T_0}\right]\left[b(1+\gamma) + \left(\frac{g-1}{g}\right)\right.$$

$$\left.\times\frac{a[1 + \gamma(g-1)/g - (1+\gamma)(T_\infty/T_0)]}{T - T_\infty}\right]. \qquad \text{(A11)}$$

This equation will remain a good approximation up to a higher temperature than will Eq. (2.42), because the ratio of the value of $g^2 J(J+1)(g-1)/g$ for the $J = \frac{7}{2}$ level to that of the $J = \frac{5}{2}$ level is 11.8 times smaller than the corresponding ratio of the $g^2 J(J+1)$ values of the two levels. In other words, the contribution of the $J = \frac{7}{2}$ level is relatively much smaller. See the discussion of Sec. III A.

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