

Paramagnetic Behavior of Polycrystalline Samarium from 300°K to 1400°K

SIGURDS ARAJS

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The paramagnetic susceptibility of polycrystalline samarium metal has been measured as a function of temperature between 300 and 1400°K. The high-temperature phase transformations do not produce noticeable discontinuities in the magnetic susceptibility, indicating that the interactions between the samarium ions are small at these temperatures. The experimental results are compared with the Van Vleck theory of paramagnetism. It appears that the energy levels of Sm^{+++} in metallic samarium differ more from those predicted by the Russell-Saunders coupling than has been realized before. Collective magnetic behaviors resulting from the interactions between the samarium ions are briefly discussed in the light of some recent low-temperature investigations.

INTRODUCTION

THE various investigations of the magnetic properties of the rare earth compounds have played a significant role in the study of the structure of atomic electron shells in the rare earth ions. The determination of the magnetic behavior of the rare earth elements themselves has been hindered by the unavailability of these metals in the pure state. However, recently rare earth metals have become accessible in relatively high purity from various sources primarily due to the pioneer work of Spedding and his collaborators on the methods of production of rare earth metals.¹ Although a considerable amount of work already has been done on various physical properties of rare earths from liquid helium to room temperatures, the behavior of these metals above room temperature is quite unexplored. Recently we have focused our attention on the magnetic susceptibilities of these elements at elevated temperatures because the low-temperature studies by various investigators have indicated that the magnetic behavior of rare earth metals in the paramagnetic state can be fairly successfully explained using a positive-ion approximation and the Van Vleck theory of paramagnetism. However, these conclusions were based on measurements made in relatively small temperature ranges. Our primary goal was to extend the magnetic susceptibility measurements with respect to the temperature and then to compare the observed magnetic behavior with the detailed predictions of the Van Vleck theory.

THEORETICAL CONSIDERATIONS

The electronic configuration of a tripositive samarium ion is $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^2 4p^6 4d^{10} 4f^5, 5s^2 5p^6$. According to the Hund rule and due to the fact that the $4f$ shell is less than half full, the energy levels of the lowest multiplet of Sm^{+++} are ${}^6H_{5/2}, {}^6H_{7/2}, {}^6H_{9/2}, {}^6H_{11/2}, {}^6H_{13/2}$, and ${}^6H_{15/2}$, where the term ${}^6H_{5/2}$ represents the ground state (Fig. 1).

Since the arrangement of the lowest energy levels of

a particular rare earth ion determines its magnetic behavior, a detailed knowledge of this distribution is of great significance. This information in principle can be obtained from the fluorescence spectra and infrared absorption. The positions of the energy levels of the ground multiplets have indeed been determined for various rare earths using this method. However, the structure of the multiplets can also be approximately calculated assuming the existence of the Landé interval rule² which states that the energy separation between two neighboring levels, having the same L and S value, is proportional to the higher J value of the pair. The symbols S , L , and J are the quantum numbers corresponding to the spin, orbital, and total angular momentum, respectively.

The first step toward the calculation of the energy levels is the determination of the width of the multiplet (ΔE). This can be done by the Goudsmit formula³

$$\Delta E = \frac{8\pi^4 me^2}{c^3 h^5} \frac{2L+1}{n^3 l(l+1)(2l+1)} Z^4, \quad (1)$$

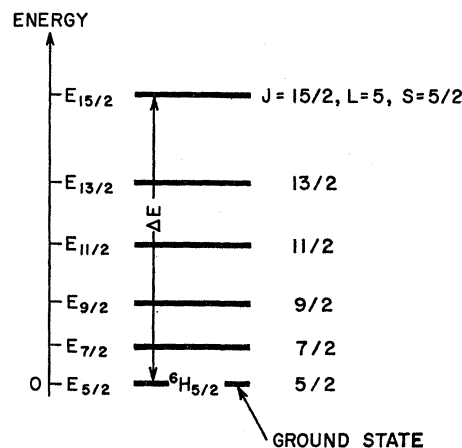


Fig. 1. Schematic representation of lowest energy multiplet of Sm^{+++} .

¹ F. H. Spedding and A. H. Daane, in *Progress in Nuclear Energy* (Pergamon Press, New York, 1956), Vol. 1, Ser. V, p. 413.

² E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (The Macmillan Company, New York, 1935), p. 193.

³ S. Goudsmit, *Phys. Rev.* **31**, 946 (1928).

where m is the mass of an electron, c the velocity of light, h the Planck constant, n the principal quantum number, l the orbital quantum number of an electron, L the total orbital quantum number for the whole electronic unit which for the rare earths is the incomplete $4f$ shell, and Z the atomic number. Since Eq. (1) was derived for a hydrogenic atom it cannot be applied to rare earth ions directly. However, we can assume that a nonhydrogenic system can be approximately represented by introducing a nuclear screening constant σ into Eq. (1), i.e., we replace Z^4 by $(Z-\sigma)^4$ and consider σ as a parameter. Using the recent values⁴ for m , e , c , and h , Eq. (1) becomes

$$\Delta E = 5.843 \frac{2L+1}{n^3 l(l+1)(2l+1)} (Z-\sigma)^4, \quad (2)$$

where the units of ΔE are in cm^{-1} .

The x-ray data of Wentzel⁵ have indicated that for rare earth ions $\sigma = 34 \pm 4$. It appears that the paramagnetic susceptibility measurements are more sensitive to σ and thus the screening constant can be more reliably determined for such studies. This has been demonstrated recently for neodymium.⁶

Once the width of the multiplet is determined, its detailed structure can be found by applying the Landé interval rule

$$E_{J-1} - E_J = AJ, \quad (3)$$

where A is a constant. The results of such calculations for tripositive samarium ion are shown in Table I. This table also shows the theoretical values obtained by Judd⁷ who, by using perturbation theory, has included in calculations the second-order corrections to the first-order positions of the energy levels. He has shown that the Landé interval is not obeyed since

$$E_{J-1} - E_J = aJ + bJ^3, \quad (4)$$

where a and b are constants. However, for most of the

rare earth ions the second-order contributions are small and thus it appears that the Russell-Saunders coupling is a moderately good approximation.

The experimental values given in Table I have been obtained by the indicated investigators using various rare earth salts.

Knowing the energy levels E_J , the paramagnetic susceptibility can be evaluated numerically using the Van Vleck theory.⁸ When the thermal energy kT is comparable with the energy intervals of the lowest multiplet, the paramagnetic susceptibility per gram can be written as

$$\chi = \frac{(N/M) \sum_J [g_J^2 \beta^2 J(J+1)/3kT + \alpha_J] (2J+1) e^{-E_J/kT}}{\sum_J (2J+1) e^{-E_J/kT}}, \quad (5)$$

where N is the Avogadro number, M the atomic weight of the particular rare earth metal, k the Boltzmann constant, T the absolute temperature, β the Bohr magneton, and

$$\alpha_J = \frac{\beta^2}{6(2J+1)} \left[\frac{F_{J+1}}{E_{J+1} - E_J} - \frac{F_J}{E_J - E_{J-1}} \right], \quad (6)$$

with

$$F_J = \frac{1}{J} [(S+L+1)^2 - J^2][J^2 - (S-L)^2]. \quad (7)$$

The quantity g_J is the Landé splitting factor, i.e.,

$$g_J = 1 + \frac{S(S+1) + J(J+1) - L(L+1)}{2J(J+1)}. \quad (8)$$

When the energy intervals of the multiplet are large in comparison with kT , Eq. (5) reduces to

$$\chi = \frac{N}{M} \frac{g_J^2 \beta^2 J(J+1)}{3kT} + \frac{N \alpha_J}{M}. \quad (9)$$

It should be mentioned here that Eq. (9) is equivalent (except for the term $N \alpha_J / M$) to that derived by Hund⁹ assuming infinite multiplet width and neglecting the second-order Zeeman term in the energy equation. The Van Vleck theory includes this second-order term which gives rise to the expression $N \alpha_J / M$ which is especially important for samarium and europium ions but is negligible for the last half of the rare earth group.

EXPERIMENTAL PROCEDURE

The magnetic susceptibilities of samarium as a function of temperature were measured using the Faraday method. The apparatus has been described in detail before.¹⁰

⁸ J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932), p. 226.

⁹ F. Hund, Z. Physik 33, 855 (1925).

¹⁰ S. Arais and D. S. Miller, J. Appl. Phys. 31, 986 (1960).

TABLE I. Energy levels of the lowest multiplet of Sm^{+++} .

Term	$E_J [\text{cm}^{-1}]$						Judd's theory ^a	Experimental
	$\sigma = 32.0$	$\sigma = 33.0$	$\sigma = 34.0$	$\sigma = 35.0$	$\sigma = 36.0$			
$^6H_{15/2}$	9683	8455	7348	6353	5463	6650	6600 ^b	6650 ^d
$^6H_{13/2}$	7042	6149	5344	4621	3973	5160	5000 ^{c, a}	4920 ^d
$^6H_{11/2}$	4754	4151	3607	3119	2682	3670	3600 ^{c, a}	
$^6H_{9/2}$	2817	2460	2138	1842	1589	2270	2300 ^{c, a}	
$^6H_{7/2}$	1232	1076	935	809	695	1030	1100 ^{c, a}	
$^6H_{5/2}$	0	0	0	0	0	0	0	

^a B. R. Judd, Proc. Phys. Soc. (London) A69, 157 (1956).

^b H. Gobrecht, Ann. Phys. 31, 755 (1938).

^c H. Gobrecht, Ann. Phys. 28, 673 (1937).

^d G. Rosenthal, Physik. Z. 40, 508 (1939).

⁴ J. A. Bearden and J. S. Thomsen, Am. J. Phys. 27, 569 (1959).

⁵ G. Wentzel, Z. Physik 33, 849 (1925).

⁶ S. Arais and D. S. Miller, Suppl. J. Appl. Phys. 31, 325S (1960).

⁷ B. R. Judd, Proc. Phys. Soc. (London) A69, 157 (1956).

TABLE II. Spectrographic analysis of samarium.

Major impurities	Amount (wt %)
Mg	0.1
Nd	0.07
Ca	0.05
Eu	0.03
Gd	<0.02
Fe	<0.005
Ti	Trace
Cu	Faint trace
Al, Ce, Co, Cr, Hf, La, Mo, Nd, Ni, Pr, Si, Ta, Tb, V, Y, Zr	Not detected

Cast polycrystalline samarium (99+%) was purchased from the Lindsay Chemical Division of the American Potash and Chemical Corporation. Results of the spectrographic analysis are given in Table II.

Three samples (designated by numbers 1, 2, and 3) were prepared from the original material. Each sample, having a mass of about 7 grams, was wrapped in a tantalum foil and enclosed in a silica capsule. Since the vapor pressure of samarium at elevated temperatures is quite high, the capsules were filled with helium gas at about 20 cm Hg pressure at room temperatures.

The magnetic susceptibility of each sample was at first measured at room temperatures. After the high-temperature studies the susceptibilities of these samples were again checked at room temperatures. This procedure showed no appreciable change in the susceptibility values, thus showing that the high vapor pressure of samarium did not influence the measured χ vs T curve.

RESULTS AND DISCUSSION

Values of the paramagnetic susceptibility of metallic samarium were obtained from the experimental magnetic susceptibility data by correcting for the diamagnetic contribution which was taken to be $-0.13 \times 10^{-6} \text{ g}^{-1} \text{ cm}^3$.¹¹ The paramagnetic behavior of samarium as a function of temperature is shown in Fig. 2. This figure also shows all the known previous investigations¹²⁻¹⁵ on metallic samarium at room temperatures. The present measurements in the neighborhood of 300°K agree satisfactorily with the room-temperature value determined by Spedding *et al.*¹³ The deviations of Lock's¹⁴ and Leipfinger's¹⁵ values from the present investigation are very possibly due to larger impurity contents in their samples. The point associated with

¹¹ H. H. Landolt and R. Börnstein, *Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie* (Springer-Verlag, Berlin, 1950), Vol. I, Part I, p. 396.

¹² W. Klemm and H. Bommer, *Z. anorg. u. allgem. Chem.* **231**, 138 (1937).

¹³ F. H. Spedding, S. Legvold, A. H. Daane, and L. D. Jennings, in *Progress in Low-Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. II, p. 368.

¹⁴ J. M. Lock, *Proc. Phys. Soc. (London)* **B70**, 566 (1957).

¹⁵ H. Leipfinger, *Physikalisches Institut der Technischen Hochschule München*, 1957, technical Report No. AFOSR-TN-57-561 (unpublished); *Z. Physik* **150**, 415 (1958).

Lock's name in Fig. 2 is only approximately correct since it was obtained from the χ vs T graph of his paper. The magnetic susceptibility of samarium measured by Klemm and Bommer¹² at room temperatures is considerably larger than those of all the other investigators. It can be expected that the cause of this difference is due to impurities. Also it should be mentioned that Klemm and Bommer used a mixture of powdered samarium and potassium chloride for their magnetic investigations. Similarly, also Leipfinger's work was done with a powdered samarium.

Samarium, which is rhombohedral at room temperatures, changes its crystal structure at about 1190°K.¹⁶ The structure below this temperature may be viewed as a series of almost close packed layers whose pseudo c/a ratio is about 1.4% smaller than for an ideal close packed structure.¹⁶ The crystal structure of samarium is more complicated than that of the other rare earth metals. It takes nine layers before the structure repeats itself. Also, there is in addition a disorder corresponding to a 180° rotation about the c axis.

The present investigation on samarium shows that the paramagnetic susceptibility does not change appreciably as the crystal structure changes. Also, there is no discontinuity in the χ vs T curve at the melting point of samarium (1325°K).¹³ These observations are similar to those found in neodymium.⁶ These facts may be explained as a result of weak interactions between the tripositive ions at elevated temperatures.

The solid curves in Fig. 2, obtained by Burrough's Datatron 205 computer, are the theoretical predictions according to the Van Vleck theory of paramagnetism. The previous work of neodymium⁶ showed that the simple theory, as discussed before for the calculations of the energy levels of the lowest multiplet, was quite

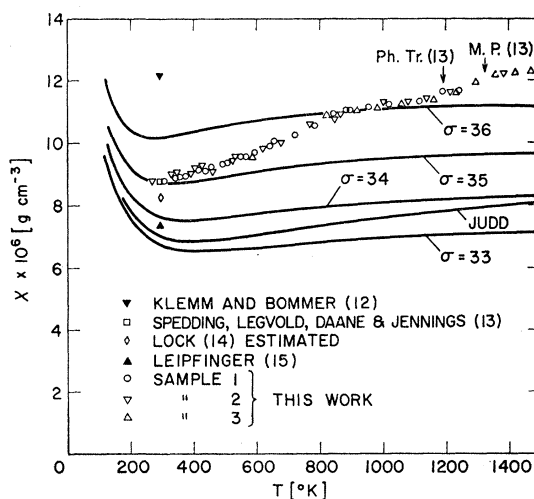


FIG. 2. Paramagnetic susceptibility of Sm as a function of temperature.

¹⁶ A. H. Daane, R. E. Rundle, H. G. Smith, and F. H. Spedding, *Acta Cryst.* **7**, 532 (1954).

satisfactory for explaining the temperature dependence of metallic neodymium. In fact, it was found that the screening constant $\sigma=35$. For samarium such a value of σ gives perfect agreement between the theoretical and experimental values of the paramagnetic susceptibility at 300°K. However, the measured temperature variation of χ for samarium is considerably larger than the simple theory predicts. It appears that these deviations result mainly from the energy level distributions used in the susceptibility calculations, although the 5*d*-electron and conduction-electron contributions may also be partially responsible. It is interesting to note that the more refined theory of Judd⁷ for finding the energy levels of the tripositive samarium ion does not help to explain the observed temperature dependence of the paramagnetic susceptibility for samarium metal. Thus, it is possible that the breakdown of the Russell-Saunders coupling in metallic samarium is larger than that used in Judd's theory, although it seems to satisfy the observed spectroscopic results in various samarium salts as indicated in Table I. Finally, it should also be emphasized that the Van Vleck theory does not include any interactions between the rare earth ions, i.e., the theoretical curves in Fig. 2 represent the magnetic behavior of systems consisting of noninteracting tripositive samarium ions with various energy level distributions.

Although this paper deals primarily with the magnetic behavior of metallic samarium above room temperatures, some comments of interest will also be made on the low-temperature properties. This region is especially interesting because the interactions between the samarium ions which are not very important at elevated temperatures become extremely important at low temperatures, giving rise to certain collective behavior. The only known work of interest on direct magnetic studies is that due to Lock.¹⁴ His data show anomalies in the $1/\chi$ vs T curve at about 100°K and 14.8°K. Lock considers 14.8°K as the Néel temperature. The magnetic susceptibility anomalies are supported also by specific heat investigations^{17,18} and recently by

electrical resistivity studies.¹⁹ Roberts,¹⁷ who measured the specific heat of samarium between 2 and 20°K, found a peak in the specific heat curve at 13.6°K, which has been confirmed by Jennings *et al.*,¹⁸ who report the anomaly at 13.8°K. In addition to this peak, Jennings *et al.* also found an anomaly in the specific heat at 105.8°K. The electrical resistivity measurements of samarium made by Colvin¹⁹ completely support the above-mentioned anomalies. Moreover, the work of Colvin *et al.*²⁰ on the electrical resistivity of heavy rare earths, where the magnetic status of these metals has been established by magnetic investigations, suggests that the two anomalies observed in metallic samarium are of magnetic origin. In fact, it appears that the Néel temperature may be 105°K and not 14.8°K as suggested by Lock. Moreover, it is tempting to consider the transition in the neighborhood of 14°K to be due to something like a ferromagnetic ordering. Although Lock's data on the magnetic susceptibility do not seem to support this picture at the present time, it may be that his sample consisting of a polycrystalline agglomerate of condensed samarium vapor on a thin tantalum sheet was not satisfactory for the studies of collective magnetic interactions. It definitely appears that the problem of the low-temperature magnetic behavior of samarium metal is not yet settled.

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¹⁷ L. D. Jennings, E. D. Hill, and F. H. Spedding, *J. Chem. Phys.* **31**, 1240 (1959).

¹⁸ L. M. Roberts, *Proc. Phys. Soc. (London)* **B70**, 434 (1957).

¹⁹ R. V. Colvin, Iowa State University, Ames, Iowa (private communication).

²⁰ R. V. Colvin, S. Legvold, and F. H. Spedding (to be published).