Magnetic Properties of Trivalent Ions of Europium and Samarium

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The magnetic susceptibilities of Eu2O3, Sm2O3 (in two crystalline modifications) and Sm2(C2O4)3·10H2O have been measured from 12 to 300° K. A strong dependence of the magnetic properties of the samarium ion on the crystalline structure of the compound in which it occurs was found. With a decrease in the effect of the crystalline field, the experimental curves of the temperature dependence of the magnetic susceptibility approximate the theoretical curve of Van Vleck for free ions. An apparatus for measuring magnetic susceptibility over a wide temperature interval is described.

I. INTRODUCTION

The investigation of the magnetic properties of the rare earth elements has played a significant role in the study of the structure of atomic electron shells. The magnetic susceptibility of the majority of the compounds of the rare earth elements satisfies the Curie law. The compounds of europium and samarium are an exception. The splitting of the deepest multiplet levels is very small for the ions of these elements. The difference in energy between the first excited level and the ground state $E_1 - E_0$ is comparable with the energy of thermal motion even at room temperatures. The magnitude of $(E_1 - E_0)/k \sim 1400$° K for samarium. As Van Vleck has shown, this must lead to intrinsic anomalies in the temperature dependence of the magnetic susceptibility. For an explanation of the magnetic properties of europium and samarium, two circumstances must be considered.

1. The smallness of the difference $E_1 - E_0$ indicates a significant effect of the quadratic term in the energy of interaction of the magnetic moment of the atom with the magnetic field. Instead of the simple Curie law for the magnetic susceptibility, there results in this case the more complicated expression

$$\chi_J = \frac{N\mu_J^2}{3kT} (J + 1) \exp \left\{- \frac{E_1}{kT} \right\} + N_0 \chi$$

in which there enters the temperature independent term $N_0 \chi$. The latter arises when account is taken of nondiagonal matrix elements of the square of the magnetic moment. In the region of low temperatures the first term predominates, and the susceptibility varies in inverse proportion to the temperature. As the temperature is increased, the susceptibility approaches a constant limit. The magnetic susceptibility of the trivalent ion of samarium must satisfy this law for low temperatures.

2. Moreover, because of the smallness of the multiplet splitting, a considerable portion of the ions are in excited states even at room temperatures. Formula (1) will be correct for such a group of ions, occurring in the equation with a given value of $J$. Van Vleck has derived the following general formula for the total susceptibility:

$$\chi = \sum_j \chi_J (2J + 1) \exp \left\{- \frac{E_J}{kT} \right\} \left\{ \sum_j (2J + 1) \exp \left\{- \frac{E_J}{kT} \right\} \right\}.$$  

The magnetic susceptibility of Eu+++ must satisfy this dependence. $E_1 - E_0$ for samarium is sufficiently large up to $\sim 150$° K this summation may be limited to only its first term. The testing of

Van Vleck's theory at the lowest possible temperatures is of very great interest. Sufficiently complete experimental results were not obtained in the works completed earlier by Wiersma and

The present work is devoted to an experimental investigation of the magnetic properties of the trivalent ions of europium and samarium at low temperatures.

2. APPARATUS AND SAMPLES

The Faraday method, based on the measurement of the force exerted on a small sample placed in an inhomogeneous field, was used in the measurement of the magnetic susceptibility.

A general view of the apparatus is schematically represented in Fig. 1. The magnetic field, in which the sample was under investigation, was produced by the electromagnet $I$. Powdered samples were placed in a quartz tube of diameter 3 mm and height 5 mm. The tube was suspended by a long quartz thread from one end of the beam of a balance which served for the measurement of the force exerted on the sample. The balance beam had an arm 3 cm in length; it was reinforced by a tension member made of bronze strip of thickness 30 $\mu$ and width 0.6 mm. Screws 6 and 7 served for the adjustment of the center of gravity and the attainment of equilibrium in the absence of the field. The balance was provided with an oil damper 8. The position of the balance was observed by the deflection of a light beam on a scale located 2 m away. The force acting on the sample was balanced by the force of interaction of the magnetic field of the compensating coil 10, fed with alternating current, on a piece of permalloy suspended from the other arm of the beam. The tube containing the sample and the counterweight of permalloy were suspended from the beam arms by quartz threads (diameter 50 $\mu$). The balance and the suspended sample were enclosed in a hermetically sealed system consisting of the cover 11 and the glass tubes 12 and 13. The lower part of the tube 13 was removable (as a section) and had at the end a copper tube 16. Calibration of the entire apparatus was done by means of standard weights, certified by the All-Union Institute of Metrology.

In order to allow the measurement of the magnetic susceptibility over a wide range of temperatures, the tube 13, in which the sample was located, was surrounded with a vacuum jacket 14. This entire system was immersed in the Dewar 15, filled with either liquid nitrogen or hydrogen. A heating coil was wound on the copper tube 16. By sending current through the heater with a vacuum of $\sim 10^{-3}$ mm Hg in the jacket, we can easily cover the two continuous temperature ranges from 20 to 90° K and from 77 to 300° K.

The temperature was measured by means of a copper-constantan thermocouple soldered to the copper tube. It was ascertained that the temperature of the sample was always sufficiently close to the temperature of the copper tube surrounding it.

The described apparatus allowed the measurement of the magnetic susceptibility over a wide temperature interval.

The sensitivity of the balance was $\sim 0.003$ mg per 1 mm deflection of the light beam. Three field intensities, from 2 to 6 kilo-oersteds, depending on the susceptibility of the sample, were used in the susceptibility measurements. With a maximum field intensity and with a sample of weight $\sim 10$ mg, the sensitivity of the arrangement was $\sim 10^{-6}$ cgsu per 1 mm deflection of the light beam. We estimate the accuracy of the determination of the absolute value of the susceptibility as 3-4%. The accuracy of the relative measurements was $\sim 1.5%$.

All the samples we investigated had the form of microcrystalline powders. Measurements were made on portions of $\sim 10$ mg, and were made on at least two portions of each compound. The majority of the compounds were kindly prepared for us by L. V. Zaozerskii and were of special purity. The quantity of impurities in the sample of $\text{Fu}_2\text{O}_3$ did not exceed 0.1% and was less than 0.01% in the samples of $\text{Sm}_2\text{O}_3$ (1) and $\text{Sm}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$. On being stored for a long time, the oxides of samarium and europium absorb carbon dioxide and water. Hence, they were all kept at a temperature of 800° C for two hours be-
fore the measurements. In the case of samarium, measurements were also made with unheated oxides. In this latter case a correction was made for the weight of the absorbed carbon dioxide and water.

3. MAGNETIC SUSCEPTIBILITY OF Eu\textsubscript{2}O\textsubscript{3}

One sample of Eu\textsubscript{2}O\textsubscript{3} was investigated. A diamagnetic correction, which we took as $-0.35 \times 10^{-6}$ cgsu, corresponding to the results of the measurement\textsuperscript{2} of the susceptibility of La\textsubscript{2}O\textsubscript{3}, was made to the measured specific susceptibility.

The temperature dependence which we obtained for the gram-atomic magnetic susceptibility of the Eu\textsuperscript{+++} ion is shown in Fig. 2. The dashed curve was given in reference 3 on the basis of values of the susceptibility at only 4 temperatures. (The experimental values are indicated by small crosses.) The results of Trapnell and Selwood\textsuperscript{3} agree sufficiently well with our results, although they drew their curve erroneously because of an insufficiency of experimental points.

At low temperatures, for which all the europium ions are in the ground state with $J = 0$, only the constant term remains in Eq. (2): $\chi_0 = N_\alpha_0$. The susceptibility actually remains constant up to $\sim 40^\circ$ K. From the magnitude of this susceptibility, $X_0$ (Eu\textsuperscript{+++}) $= 8.42 \times 10^{-3}$ cgsu, the difference in energy between the ground and first excited levels can be calculated. The value which we obtained, $E_1 - E_0 = 250$ cm$^{-1}$, lies essentially lower than the value of 400 cm$^{-1}$ obtained from spectroscopic data.\textsuperscript{5} However, it agrees well with the value calculated by Van Vleck for a shielding constant of $\alpha = 34$. It should also be noted that the value of the overall width of the multiplet $\sim 5200$ cm$^{-1}$ calculated from our value of $E_1 - E_0$ coincides with the value 5000 cm$^{-1}$ obtained from spectroscopic results.

The number of ions in the ground state decreases with an increase in temperature, and the susceptibility which depends on these ions falls according to the law $\chi = N_\alpha_0 / (1 + 3 \exp! - (E_1 - E_0)/kT)$. The overall susceptibility falls somewhat more slowly, since the ions which are in excited states also contribute to the susceptibility. Our results agree quite well with Van Vleck’s formula (2) if we take $E_1 - E_0 = 250$ cm$^{-1}$. A small discrepancy is observed only in the region $60 - 100^\circ$ K, where the values of the susceptibility lie somewhat below the theoretical curve.

4. MAGNETIC PROPERTIES OF THE TRIVALENT ION OF SAMARIUM

The magnetic properties of Sm\textsuperscript{+++} were studied in two compounds: Sm\textsubscript{2}O\textsubscript{3} and Sm\textsubscript{2}(C\textsubscript{2}O\textsubscript{4})\textsubscript{3} \cdot 10H\textsubscript{2}O. Two samples of Sm\textsubscript{2}O\textsubscript{3} were investigated: one sample (I) a product of the 'ahlbaum firm, the purity of which, according to the results of a spectroscopic analysis,\textsuperscript{*} was not less than 99.0%, and the other sample (II) prepared by I. N. Zaozeretskii. The latter sample was of very high purity ($\sim 99.99\%$). Investigations were carried out with both samples, both before heating them and after heating them.

Preliminary experiments on the magnetic susceptibility of both samples of Sm\textsubscript{2}O\textsubscript{3} gave a basis for supposing that we had to do with two crys-

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{fig2}
\caption{Temperature dependence of the atomic magnetic susceptibility of the Eu\textsuperscript{+++}; the continuous curve is according to the theory of Van Vleck\textsuperscript{1,4}, the points + are the results of Trapnell and Selwood\textsuperscript{3}, and the points O are the results of the present work.}
\end{figure}

\begin{center}
As is clear from Fig. 2 our results agree quite well with the theoretical conclusions of Van Vleck\textsuperscript{1,4}.
\end{center}


\textsuperscript{*} The authors extend their thanks to S. A. Borovik, who carried out the spectral analysis of this compound.

\textsuperscript{5} M. A. El’iashevich, Spectra of the Rare Earths, 1953.
talline modifications. X-ray photographs* confirmed that for sample I the crystalline structure of the heated compound differed essentially from the structure of the unheated compound, while for sample II both structures were nearly the same. It is known from the literature (see, for example, reference 6) that at room temperatures $\text{Sm}_2\text{O}_3$ has a body-centered cubic lattice (of the type of $\text{Mn}_2\text{O}_3$) with 16 molecules in the elementary cell. A new crystalline modification is formed at a temperature of 720º C. This modification has been little studied; it has a pseudotrigonal structure. Evidently in the freshly heated sample I we were concerned with the supercooled high temperature pseudotrigonal modification of $\text{Sm}_2\text{O}_3$. The remaining forms had the cubic structure. It should be emphasized that in the very pure compound (sample II) supercooling does not occur, and we are at all times, both before and after the heating, concerned only with the equilibrium low temperature modification. We assume that the presence of impurities in sample I facilitated the formation of the high temperature modification.

The results of the investigation of the temperature dependence of the magnetic susceptibility of both samples are given in Fig. 3. Within the limits of error of the measurements, all the points lie on two separate curves. Curve 2 corresponds to the results obtained for the heated sample I, that is, for the pseudotrigonal structure of $\text{Sm}_2\text{O}_3$. The results obtained at Leyden in 1936 are also put with this curve. The results obtained for both unheated samples describe curve 1. The results obtained for the heated sample II also coincide with them. Thus this curve corresponds to the cubic modification of $\text{Sm}_2\text{O}_3$.

Both curves agree qualitatively with the theoretical curve of Van Vleck, although the quantitative discrepancies, especially at low temperatures, are very significant. It would be natural to suggest that these discrepancies depend on the effect of the crystalline field (see below). Hence it would be desirable to carry out an investigation of the magnetic properties of $\text{Sm}^{+++}$ in another compound, where the effect of the crystalline field would be smaller. Samarium oxalate ($\text{Sm}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$), a salt favorably distinguished by its great number of molecules of water of crystallization and the constancy of their number, was chosen. The $\text{H}_2\text{O}$ molecules surround the Sm ion in the crystal of the salt and significantly lower the inhomogeneous crystalline field acting on the ion. The results obtained for the sample of $\text{Sm}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ are also given in Fig. 3 (curve 3). They much more nearly coincide with the theoretical curve, deviating from it by only 20% for 20º K.

With the aid of the value of $\chi(\text{Sm}^{+++}) = 1.07 \times 10^{-3}$ cgsu (at 293º K), obtained for $\text{Sm}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ by formula (2), the difference in energy between the lowest levels of the $\text{Sm}^{+++}$ multiplet was calculated. The value $E_1 - E_0 = 1020$ cm$^{-1}$ (equivalent to 1470º K) obtained agrees sufficiently well with the value 1100 cm$^{-1}$ obtained from

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* The X-ray photographs of the samples were taken by V. P. Tarasova and D. I. Graevskaia, with the kind assistance of V. I. Iveronova. The authors express to them their deepest thanks.

spectroscopic results. It lies between the two values (1070 cm\(^{-1}\) and 932 cm\(^{-1}\)) theoretically calculated by Van Vleck for the two shielding constants \(\sigma = 33\) and \(\sigma = 34\).

The significant deviations of our results for the magnetic susceptibility of the two modifications of \(\text{Sm}_2\text{O}_3\) from the theoretical curve for free \(\text{Sm}^{++}\) ions must be explained by the effect of the crystalline field. The question of the properties of the crystalline field on the magnetic properties of the ions of the rare earth elements has been considered in a number of theoretical investigations. In particular, the effect of the crystalline field on the magnetic properties of \(\text{Sm}^{++}\) is the subject of the present investigation.

The magnetic splitting of the levels in \(\text{Sm}^{++}\) due to the crystalline field is characterized by the effective magnetic quantum numbers \(M_i\). The magnetic susceptibility is given by the formula:

\[
\chi = \frac{N g_i^2 \mu_0^2}{k T} \frac{M_{i\text{eff}}^2 + M_{i\text{eff}}^2 \exp(-\Delta W_i/kT) + M_{i\text{eff}}^2 \exp(-\Delta W_2/kT)}{1 + \exp(-\Delta W_1/kT) + \exp(-\Delta W_2/kT)} + N \alpha,
\]

where \(\Delta W_1\) and \(\Delta W_2\) are the energy differences between the two corresponding upper and lower sublevels. The values of the effective magnetic quantum numbers of each of the sublevels are obtained as a linear combination of the magnetic quantum numbers of the free ion

\[
M_{i\text{eff}} = \sum_M |z_M^i| M,
\]

where the \(z_M^i\) are the coefficients in the expansion of the wave functions corresponding to the \(i\)th sublevel, for the wave functions of the ion in a field of cylindrical symmetry. The general solution of the problem of the calculation of the particular form of formula (3) requires a knowledge of the symmetry of the crystalline field and the form of its potential. However, in many cases it may be assumed that the \(M_{i\text{eff}}\) are approximately equal to the corresponding values of the magnetic quantum number of the free ion. For \(\text{Sm}^{++}\) one should put into the formula the respective values:

\[M_1 = \pm 1/2, \quad M_2 = \pm 3/2, \quad M_3 = \pm 5/2.\]

By comparing the resulting formula with the experimental results, we determined the values of the parameters \(\Delta W_1\) and \(\Delta W_2\) which occur in the formula. For the cubic modification of \(\text{Sm}_2\text{O}_3\) we obtained: \(\Delta W_1 = 0\) and \(\Delta W_2 = 52 \text{ cm}^{-1}\) (equivalent to 73° K). For the pseudotrigonal modification of \(\text{Sm}_2\text{O}_3\) we found \(\Delta W_1 = 20 \text{ cm}^{-1}\) (29° K) and \(\Delta W_2 = 150 \text{ cm}^{-1}\) (218° K).

Our experimental results are shown in the graph of Fig. 4, where the coordinates are \(1/\chi\) and \(T\). Curve 4 of this graph corresponds to Van Vleck's formula (1), curves 1 and 3 were calculated according to formula (3), using the values of the constants introduced above. Although a rather rough assumption on the replacement of \(M_{i\text{eff}}\) by \(M\) was made in the construction of these curves, a consideration of them gives a basis for some general conclusions. First, when the corresponding set of constants is used in Eq. (3), it will describe with a sufficient degree of accuracy the results obtained for the magnetic susceptibility of the samarium ion in various compounds. Second, for all the compounds of samarium which were investigated, the value of the effective magnetic quantum number corresponding to the lower sublevel must be less than the \(M_{i\text{eff}}\) corresponding to the upper sublevel, since only in this case do we obtain curves situated above the curves for the free ions. Giesekus, in his calculations on the splitting of the levels in \(\text{Sm}_2\text{(BrO}_3\text{)}_3\cdot9\text{H}_2\text{O}\) ar-

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CONCLUSIONS

In summing up the work reported, we may draw the following general conclusions:

1. The temperature dependence of the magnetic susceptibility of Eu$_2$O$_3$ agrees sufficiently well with the theoretical dependence of Van Vleck. The small deviation in the region 40 - 80° K may be explained by the splitting up of the first excited level, since this must lead to the decrease in susceptibility beginning at lower temperatures.

2. The magnetic properties of the Sm$^{+++}$ ion (especially at low temperatures) depend very strongly on the crystalline lattice in which it is found.

3. When a small amount of impurities is present, samarium oxide which has been heated to 800° C keeps the crystalline structure of the high temperature phase when it is cooled to room temperature. The magnetic properties of the equilibrium and supercooled phases of Sm$_2$O$_3$ are essentially different at low temperatures. The deviation of the temperature dependence of the magnetic susceptibility of both crystalline forms of Sm$_2$O$_3$ from Van Vleck's theory for free ions may be qualitatively explained by the splitting of the ground state of Sm$^{+++}$ in the field of the lattice.
4. The temperature variation of the magnetic susceptibility of samarium oxalate, for which the effect of the crystalline field should be small, is very close to the theoretical curve for free ions.

5. Energy differences between the first excited state and the ground state were calculated from the magnetic data. The values obtained (250 cm\(^{-1}\) for Eu\(\text{+++}\) and 1020 cm\(^{-1}\) for Sm\(\text{+++}\) agree quite well with spectroscopic results.

In conclusion, the authors wish to express their deep gratitude to Professor P. G. Strelov for his constant interest in the work and to Professor I. N. Zaozerskii, who kindly prepared the samples and gave us a number of valuable suggestions.

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