

## Paramagnetic Susceptibility of Eu<sub>2</sub>O<sub>3</sub> from 300° to 1300°K

Sigurds Arajs and R. V. Colvin

Citation: *Journal of Applied Physics* **35**, 1181 (1964); doi: 10.1063/1.1713589

View online: <http://dx.doi.org/10.1063/1.1713589>

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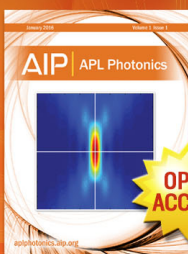
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# Paramagnetic Susceptibility of $\text{Eu}_2\text{O}_3$ from 300° to 1300°K

SIGURDS ARAJS AND R. V. COLVIN

*Edgar C. Bain Laboratory for Fundamental Research, United States Steel Corporation  
Research Center, Monroeville, Pennsylvania*

(Received 2 October 1963)

The magnetic susceptibility of  $\text{Eu}_2\text{O}_3$  has been studied as a function of temperature between 300° and 1300°K. The results can be satisfactorily explained by the Van Vleck theory of paramagnetism with Judd's energy levels of free  $\text{Eu}^{3+}$  ions.

## INTRODUCTION

THE ion  $\text{Eu}^{3+}$  has an electronic configuration  $4f^6$  which gives rise to seven energy levels,  ${}^7F_0$ ,  ${}^7F_1$ ,  ${}^7F_2$ ,  ${}^7F_3$ ,  ${}^7F_4$ ,  ${}^7F_5$ ,  ${}^7F_6$ , which form the lowest energy multiplet,  ${}^7F_0$  being the ground state. Knowing these, one can predict the temperature behavior of certain physical properties (magnetic susceptibility, paramagnetic moment, gyromagnetic ratio, localized electron specific heat) for a system made up of free or almost free  $\text{Eu}^{3+}$  ions. These ions are particularly interesting because the energy-level separations are comparable with the thermal energy available at elevated temperatures. Thus the role of temperatures on the above-mentioned properties is much more noticeable in  $\text{Eu}^{3+}$  systems than for other rare-earth ions. Metallic Eu is an anomalous rare-earth metal because it possesses seven  $4f$  electrons and hence does not have the close-spaced level structure associated with free  $\text{Eu}^{3+}$  ions. However, in  $\text{Eu}_2\text{O}_3$  the ions are tripositive and, as demonstrated by older studies,<sup>1,2</sup> are quite free. Therefore, we decided that it would be of some interest to perform magnetic susceptibility measurements in  $\text{Eu}_2\text{O}_3$  as a function of temperature and then to apply the Van Vleck theory<sup>1</sup> with Judd's energy levels<sup>3</sup> to the experimental data. The results of this study are presented in this paper.

## EXPERIMENTAL CONSIDERATIONS

The sesquioxide  $\text{Eu}_2\text{O}_3$  used in this investigation was purchased from the Research Chemicals Division of Nuclear Corporation of America. Results of a partial analysis are given in Table I. About 1.5 g of powdered  $\text{Eu}_2\text{O}_3$  was sealed into an evacuated silica capsule. The magnetic susceptibility was measured using the apparatus described elsewhere.<sup>4,5</sup> The diamagnetic contribution of the silica capsule was determined separately. This correction was then applied to the measured susceptibilities, thus giving the total magnetic susceptibility of the oxide. The measurements were found to be independent of heating and cooling rates of the sample.

X-ray studies by Dr. Henry Chessin of this Labora-

tory showed that the  $\text{Eu}_2\text{O}_3$  whose magnetic properties were investigated possessed the cubic ( $\text{Mn}_2\text{O}_3$ -type) structure. According to the most recent work on the polymorphism of the rare-earth sesquioxides,<sup>6</sup> the cubic form of  $\text{Eu}_2\text{O}_3$  is stable up to 1373°K, at which it transforms to the monoclinic ( $\text{Sm}_2\text{O}_3$ -type) structure. Since our measurements did not exceed 1325°K, all the magnetic data presented in this report refer to the cubic modification. The lattice parameter of  $\text{Eu}_2\text{O}_3$  used in this work was found to be 10.868 Å at room temperature. This value compares favorably with that quoted by Gschneidner,<sup>7</sup> i.e.,  $10.863 \pm 3$  Å.

## RESULTS AND DISCUSSION

The paramagnetic part,  $\chi_{\text{para}}(\text{Eu}_2\text{O}_3)$ , of the measured mass magnetic susceptibility of  $\text{Eu}_2\text{O}_3$ ,  $\chi(\text{Eu}_2\text{O}_3)$ , was obtained by subtracting the diamagnetic contribution,  $\chi_{\text{diam}}(\text{Eu}_2\text{O}_3)$ , from the measured susceptibility. The diamagnetic part was calculated from the equation

$$\chi_{\text{diam}}(\text{Eu}_2\text{O}_3) = [2\chi_{\text{diam}}^{\text{mole}}(\text{Eu}^{3+}) + 3\chi_{\text{diam}}^{\text{mole}}(\text{O}^{2-})] / M(\text{Eu}_2\text{O}_3), \quad (1)$$

where  $\chi_{\text{diam}}^{\text{mole}}(\text{Eu}^{3+})$  and  $\chi_{\text{diam}}^{\text{mole}}(\text{O}^{2-})$  are the diamagnetic susceptibilities per mole of  $\text{Eu}^{3+}$  and  $\text{O}^{2-}$  ions, respectively, and  $M(\text{Eu}_2\text{O}_3)$  is the molecular weight of  $\text{Eu}_2\text{O}_3$ . Using the values<sup>3</sup>  $\chi_{\text{diam}}^{\text{mole}}(\text{Eu}^{3+}) = -20 \times 10^{-6} \text{ mole}^{-1} \text{ cm}^3$  and  $\chi_{\text{diam}}^{\text{mole}}(\text{O}^{2-}) = -12 \times 10^{-6} \text{ mole}^{-1} \text{ cm}^3$  one finds  $\chi_{\text{diam}}(\text{Eu}_2\text{O}_3) = -0.22 \times 10^{-6} \text{ g}^{-1} \text{ cm}^3$ . It is convenient to convert the quantity  $\chi_{\text{para}}(\text{Eu}_2\text{O}_3)$  to the mass paramagnetic susceptibility of  $\text{Eu}^{3+}$  ions  $\chi_{\text{para}}(\text{Eu}^{3+})$ . This can be done by means of the equation

$$\chi_{\text{para}}(\text{Eu}^{3+}) = \frac{1}{2} [M(\text{Eu}_2\text{O}_3) / M(\text{Eu})] \chi_{\text{para}}(\text{Eu}_2\text{O}_3), \quad (2)$$

where  $M(\text{Eu})$  is the atomic weight of Eu. Thus, the experimental susceptibility data on  $\text{Eu}_2\text{O}_3$  can be compared with the theoretical mass paramagnetic suscepti-

TABLE I. Partial analysis of  $\text{Eu}_2\text{O}_3$ .<sup>a</sup>

Calcium	0.02%
Gadolinium	0.02%
Samarium	0.02%

<sup>a</sup> Other elements detected: Al, Cr, Mg, Mn, Fe, Si, Yb.

<sup>1</sup> J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932).

<sup>2</sup> P. W. Selwood, *Magnetochemistry* (Interscience Publishers, Inc., New York, 1956), 2nd ed.

<sup>3</sup> B. R. Judd, *Proc. Phys. Soc. (London)* **A69**, 157 (1956).

<sup>4</sup> S. Aarj and D. S. Miller, *J. Appl. Phys.* **31**, 986 (1960).

<sup>5</sup> S. Aarj and R. V. Colvin, *J. Phys. Chem. Solids* **24**, 1233 (1963).

<sup>6</sup> I. Warshaw and R. Roy, *J. Phys. Chem.* **65**, 2048 (1961).

<sup>7</sup> K. A. Gschneidner, Jr., *Rare Earth Alloys* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1961).

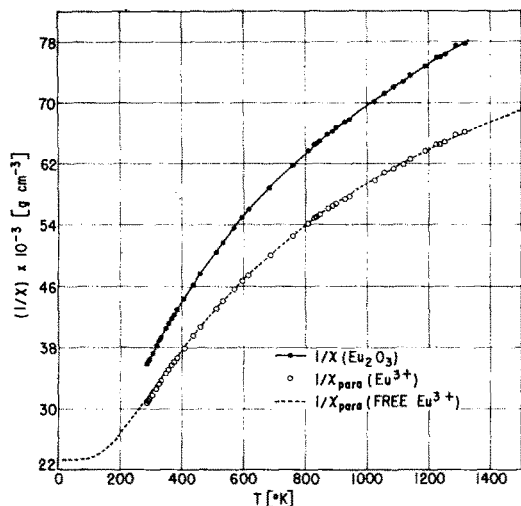


FIG. 1. Inverse magnetic susceptibility of  $\text{Eu}_2\text{O}_3$  in comparison with the theoretical prediction.

bility of free  $\text{Eu}^{3+}$  ions,  $\chi_{\text{para}}(\text{free Eu}^{3+})$ , as predicted by Van Vleck theory<sup>1</sup>:

$\chi_{\text{para}}(\text{free Eu}^{3+})$

$$= \left\{ \frac{N}{M(\text{Eu})} \sum_J \left[ \frac{q^2 \beta^2 J(J+1)}{3kT} + \alpha \right] (2J+1) e^{-(E_J/kT)} \right\} / \sum_J (2J+1) e^{-(E_J/kT)}, \quad (3)$$

where  $N$  is the Avogadro number,  $k$  the Boltzmann constant,  $T$  the absolute temperature,  $\beta$  the Bohr magneton number,  $J$  the quantum number associated with the total angular momentum of the incomplete  $4f$  shell, and  $E_J$  the energy levels of the lowest multiplet for a free  $\text{Eu}^{3+}$  ion. The quantity  $\alpha$  is given by the equation

$$\alpha = \frac{\beta^2}{6(2J+1)} \left[ \frac{F_{J+1}}{E_{J+1} - E_J} - \frac{F_J}{E_J - E_{J-1}} \right], \quad (4)$$

with

$$F_J = (1/J)[(S+L+1)^2 - J^2][J^2 - (S-L)^2]. \quad (5)$$

Finally, the symbol  $g$  in Eq. (3) represents the Landé splitting factor, i.e.,

$$g = 1 + [S(S+1) + J(J+1) - L(L+1)] / 2J(J+1), \quad (6)$$

where  $S$  and  $L$  are the quantum numbers of the total spin and orbital angular momentum of the  $4f$  electrons of  $\text{Eu}^{3+}$  ion. For  $\text{Eu}^{3+}$  ions,  $S=3$  and  $L=3$ , and thus  $J$  can have values 0, 1, ..., 6.

In order to evaluate the susceptibility  $\chi_{\text{para}}(\text{free Eu}^{3+})$  one needs to know the energy levels  $E_J$ . These have been calculated theoretically by Judd.<sup>3</sup> The theoretical values of  $\chi_{\text{para}}(\text{free Eu}^{3+})$  were calculated according to Eqs. (3)–(6) with Judd's energy levels. The plot of the inverse of these,  $1/\chi_{\text{para}}(\text{free Eu}^{3+})$ , is shown in Fig. 1 as a broken curve. The closed points represent the measured

TABLE II. Comparison between measured magnetic susceptibility values of  $\text{Eu}_2\text{O}_3$  at 293°K according to various investigators.

Investigation	$\chi(\text{Eu}_2\text{O}_3) \times 10^6 [\text{g}^{-1} \text{cm}^3]$
Urbain <sup>a</sup>	28.9
Cabrera and Duperier <sup>b</sup>	26.6
Sucksmith <sup>c</sup>	26.1
Selwood <sup>d</sup>	31.3
Trapnell and Selwood <sup>e</sup>	29.0
Borovik-Romanov and Kreines <sup>f</sup>	~29.3
This study	27.4

<sup>a</sup> See Ref. 10.

<sup>b</sup> See Ref. 11.

<sup>c</sup> See Ref. 12.

<sup>d</sup> See Ref. 13.

<sup>e</sup> See Ref. 14.

<sup>f</sup> See Ref. 15.

inverse magnetic susceptibility of  $\text{Eu}_2\text{O}_3$ ; the open points give the inverse paramagnetic susceptibility of  $\text{Eu}^{3+}$  ions in  $\text{Eu}_2\text{O}_3$ , obtained by using Eqs. (1) and (2). One can clearly see from Fig. 1 that the agreement between the theoretical curve and the points derived from experimental results (open points) is quite satisfactory. This indicates that the  $4f$  electrons of  $\text{Eu}^{3+}$  ions in  $\text{Eu}_2\text{O}_3$  at elevated temperatures are not significantly influenced by the electric crystalline fields. Prior to the calculations by Judd the standard technique for determining the energy levels of the ground multiplets was to use the nuclear screening method. That is, one calculated the width of the energy-level multiplet from the modified Goudsmit formula and the detailed level distribution from the Landé interval rule. The nuclear screening constant  $\sigma$ , taken to be somewhere between 33 and 35, was used as a parameter which fixed the width of the multiplet. The energy-level distribution for  $\sigma=32, 33, \dots, 36$  of  $\text{Eu}^{3+}$  ions have been tabulated elsewhere.<sup>8</sup> Also we have performed the paramagnetic susceptibility calculations based on these energy levels.<sup>9</sup> However, due to the satisfactory agreement between the experimental data and the theoretical values implied by the Judd levels of  $\text{Eu}^{3+}$  ions, it was felt that the comparison with the theory of the  $\sigma$  method was not needed.

Finally, we would like to review briefly the older magnetic susceptibility results on  $\text{Eu}_2\text{O}_3$ . According to our best knowledge, the susceptibility of  $\text{Eu}_2\text{O}_3$  has been studied before us by Urbain,<sup>10</sup> Cabrera, and Duperier,<sup>11</sup> Sucksmith,<sup>12</sup> Selwood,<sup>13</sup> Trapnell, and Selwood,<sup>14</sup> and Borovik-Romanov and Kreines.<sup>15</sup> These studies have

<sup>8</sup> R. V. Colvin, S. Arajs, and J. M. Peck, Phys. Rev. **122**, 14 (1961).

<sup>9</sup> S. Arajs, R. V. Colvin, and R. W. Whitmore, "Paramagnetic Susceptibility and Bohr Magnetron Numbers of Free Tripositive Rare Earth Ions" (unpublished).

<sup>10</sup> G. Urbain, Compt. Rend. **147**, 1286 (1908).

<sup>11</sup> B. Cabrera and A. Duperier, Compt. Rend. **188**, 1640 (1929).

<sup>12</sup> W. Sucksmith, Phil. Mag. **14**, 1115 (1932).

<sup>13</sup> P. W. Selwood, J. Am. Chem. Soc. **55**, 4869 (1933).

<sup>14</sup> B. M. W. Trapnell and P. W. Selwood, Nature **169**, 840 (1952).

<sup>15</sup> A. S. Borovik-Romanov and N. M. Kreines, Zh. Eksperim. i Teor. Fiz. **29**, 790 (1955) [English transl.: Soviet Phys.—JETP **2**, 657 (1956)].

been made over quite limited temperature ranges. Sucksmith<sup>12</sup> measured the magnetic susceptibility of  $\text{Eu}_2\text{O}_3$  between 456° and 946°K while the work of Cabrera and Duperier<sup>11</sup> extends to 873°K. The investigation by Selwood covers the temperatures between 83° and 373°K and that by Trapnell and Selwood from 20° to 298°K. The most recent work on the magnetic properties of  $\text{Eu}_2\text{O}_3$  is by Borovik-Romanov and Kreines<sup>15</sup> who performed their measurements from 12° to 300°K. Table II presents the measured values of the magnetic susceptibility of  $\text{Eu}_2\text{O}_3$  at 293°K according to the above-mentioned investigators. The value attributed to Trapnell and Selwood was obtained by interpolating their  $\chi(\text{Eu}_2\text{O}_3)$  values at 195° and 298°K. The approximate

susceptibility due to Borovik-Romanov and Kreines was estimated from Fig. 2 of Ref. 15 by applying their diamagnetic correction ( $-0.35 \times 10^{-6} \text{ g}^{-1} \text{ cm}^3$ ). One can see from Table II that there is some scattering in the values of  $\chi(\text{Eu}_2\text{O}_3)$  at 293°K as determined by various investigators. These variations are very likely due to impurities present in  $\text{Eu}_2\text{O}_3$ .

#### ACKNOWLEDGMENTS

The authors are grateful to W. Rall and R. P. L. Hartley of the Applied Research Laboratory of United States Steel Corporation for performing the spectroscopic analysis of  $\text{Eu}_2\text{O}_3$  sample used in this investigation.

## Spectrophotometric Determination of Chromium Concentration in Ruby

D. M. DODD, D. L. WOOD, AND R. L. BARNES

*Bell Telephone Laboratories, Inc., Murray Hill, New Jersey*

(Received 16 August 1963; and in final form 11 November 1963)

A spectrophotometric method for determining the concentration of chromium in oriented and unoriented single ruby crystals is described. It makes use of the absorption coefficients for the blue and green bands and for the red lines at  $\sim 300^\circ\text{K}$ . The coefficients are based on concentration data obtained by three independent methods.

#### INTRODUCTION

AT the present time, chromium-doped  $\alpha$ -alumina is widely used, for example in optical and microwave masers, and it is often required to determine the concentration of chromium in the finished single crystal. This can be done nondestructively and with considerable accuracy by spectrophotometric methods once the absorption coefficients have been determined. Because of the variation of absorption with crystal orientation and with the polarization of the incident radiation, it is necessary to take such factors into account in the spectrophotometric analysis. It is, perhaps, not generally appreciated that the determination of chromium content can be made on randomly oriented crystal sections if polarized radiation is used. Since this is very convenient, the purposes of this contribution are to describe the method and report the relevant absolute absorption coefficients.

#### MEASUREMENT METHOD FOR RANDOMLY ORIENTED CRYSTALS

It is well known that chromium-doped  $\alpha$ -alumina is uniaxial and exhibits optical absorption anisotropy.<sup>1,2</sup> Therefore, it has two absorption coefficients at each frequency, one for the ordinary ray ( $E \perp C_3$  axis) and

one for the extraordinary ray ( $E \parallel C_3$  axis). In an arbitrarily oriented plane-parallel section such as that shown in Fig. 1, the optic axis makes an angle  $\theta$  with the plane of the section. Between crossed polarizers, the sample will have two extinction directions, one in the direction of the projection of the optic axis on the plane and the other perpendicular to that direction. When examined with one polarizer, the crystal will have a more purplish hue when the electric vector is perpendicular to the direction of the projection of the optic axis on the plane. Let the absorbance ( $\log I_0/I$ ), at a particular frequency for plane-polarized radiation falling normal to the section surfaces, be denoted as  $A_{11}$

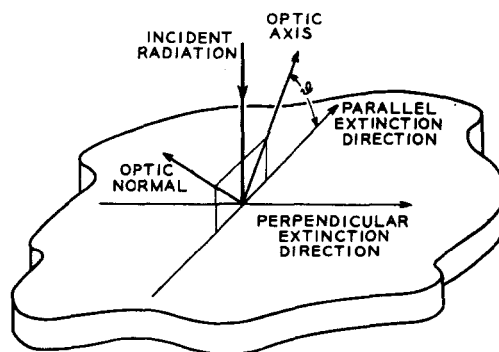


FIG. 1. Arbitrarily oriented plane-parallel section of ruby.

<sup>1</sup> S. Sugano and Y. Tanabe, *J. Phys. Soc. Japan* **13**, 880 (1958).

<sup>2</sup> D. S. McClure, *J. Chem. Phys.* **36**, 2757 (1962).