MAGNETIC SUSCEPTIBILITY OF $Eu_2(WO_4)_3$ SINGLE CRYSTALS

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The molar magnetic susceptibility of $Eu_2(WO_4)_3$ single crystals for the three principal crystallographic directions in the temperature range 4.2–900 K has been measured. The observed anisotropy has been attributed to a crystal-field effect. The average molar susceptibility is shown to follow the theoretical curve for Eu^{3+}.

1. Introduction

Magnetic properties of europium and samarium ions are unique among the rare-earths [1, 2]. They do not obey Hund's rule and the usual Curie–Weiss law [2]. The discrepancies between the theoretical and the experimental values of the magnetic susceptibility are removed by the inclusion of the second-order Zeeman effect [2]. For the last few years we have been studying the transport and magnetic properties of rare-earth tungstates [3–5]. This paper reports our study regarding the magnetic susceptibility of $Eu_2(WO_4)_3$ single crystals in all three principal crystallographic directions from 4.2 to 900 K.

$Eu_2(WO_4)_3$ is a semitransparent material with X-ray density of 7.37 g cm^{-3} and a melting point [6] between 1160 and 1260°C. It has a monoclinic structure with unit-cell dimensions $a = 7.676 \pm 0.003$ Å, $b = 11.463 \pm 0.003$ Å, $c = 11.396 \pm 0.005$ Å and $\beta = 109.63 \pm 0.04°$. It belongs to space group C2 (C_{2h}^6) with four molecules per unit cell. The lattice can also be looked upon in pseudo-orthorhombic form [7] with unit-cell dimensions $a_2 = 7.676$ Å, $b_2 = 11.463$ Å, $c_2 = 21.468$ Å and $\beta = 90.06°$. This unit cell has a volume of twice that of the monoclinic unit cell and belongs to the F 2/d space group.

2. Material and experimental techniques

Single-crystal chips of $Eu_2(WO_4)_3$ were procured from M/S Semi-Element (USA). They have not quoted any specific impurity content but have claimed a purity of 99.9%. The crystal structure was checked by X-ray diffraction techniques.

The magnetic susceptibility was measured [8] with a SQUID magnetometer at low temperatures (4.2–300 K). In this method the crystal was mounted on a quartz rod in specific orientation using the technique of Laue-photography. The performance of the SQUID is based on the concept of the magnetic flux in a superconducting ring and on Josephson tunneling through a "weak link" between two superconductors. A commercially available device has been utilized in a superconducting flux transformer which is placed in a superconducting magnet for the magnetization of the samples. The persistent current used in the superconducting coil was 600 mA. This corresponds to a magnetic field of the order of few gauss. The same value of persistent current has been used in all these measurements. The sample is moved through pick-up coils one by one using air pressure and the flux change is detected by the SQUID magnetometer. Above 300 K the susceptibility was measured using Faraday's method [9], employing a large magnet with typical pole pieces and a sensitive magnetic balance. The details of the procedure are described elsewhere [8].

3. Results and discussion

The inverse gram mole magnetic susceptibilities $(\chi_m)^{-1}$ of the single-crystals of $Eu_2(WO_4)_3$ in all the three crystallographic directions are shown in the temperature range from 4.2 to 300 K in fig. 1 and from 100 to 900 K in fig. 2. From figs. 1 and 2 the average value of χ_m was obtained and its variation with T is shown in fig. 3. This can be taken as the value for a powdered sample of $Eu_2(WO_4)_3$.

The only magnetic ion in $Eu_2(WO_4)_3$ is trivalent europium (Eu^{3+}). It has a nonmagnetic ground state ($J = 0$). Also the separation between its multiplet levels [1, 2] is less than kT below 300 K. Such ions are called Van Vleck ions. The magnetic susceptibility of these ions was first evaluated by Van Vleck and is given by the following expression:

$$\chi = \frac{\sum_{-J}^{+J}(2J + 1)\,\chi_J \exp\,(-E_J/2kT)}{\sum_{-J}^{+J}(2J + 1)\exp\,(-E_J/2kT)}, \qquad (1)$$

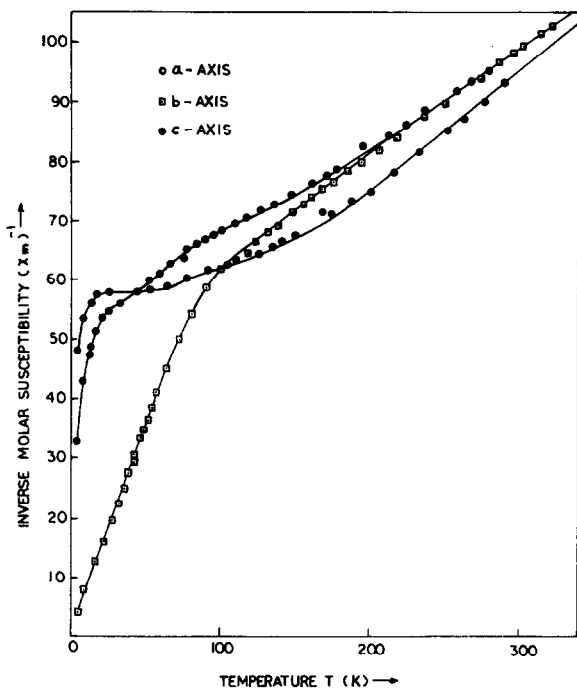where E_J is the energy and χ_J is the corresponding magnetic susceptibility for the Jth multiplet levels.

Fig. 1. Variation of the inverse molar magnetic susceptibility $(\chi_m)^{-1}$ vs. T for $Eu_2(WO_4)_3$ single crystals from 4.2 to 300 K.
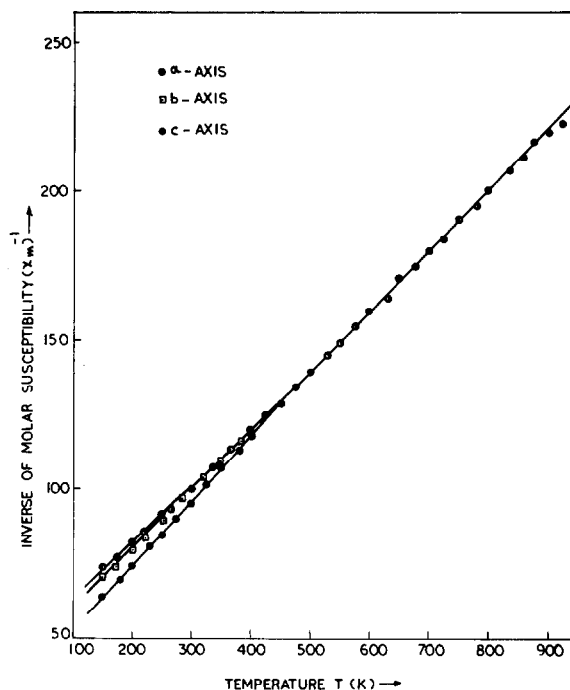

Fig. 2. Variation of the inverse molar magnetic susceptibility $(\chi_m)^{-1}$ with temperature T for $Eu_2(WO_4)_3$ single crystals from 100 to 900 K.

The numerical value of χ at different temperatures was evaluated by Frank [2]. Later, assuming simple spin—orbit interaction, the variation of χ with T for Eu^{3+} ions was evaluated by several workers [10–13]. It has been estimated that the value of spin—orbit interaction energy [13] (Δ) for Eu^{3+} ions is about 500 K.

We have evaluated the value of the susceptibility at different temperatures taking the number of Eu^{3+} ions the same as in one mole of $Eu_2(WO_4)_3$ using eq. (1). The theoretical curve obtained is shown in fig. 3. It is seen from this figure that there is a considerable difference between the theoretical and the experimental values. Also, at low temperatures the theoretical curve yields a constant value of susceptibility below 100 K. No such constancy has been observed in the experimental curve. This difference between the theoretical and the experimental curves may be due to impurities. An EPR spectrum of this crystal, taken at room temperature, gives a differential peak corresponding to Eu^{2+} ions. An estimate from this spectrum gives a concentration of about 0.2% of
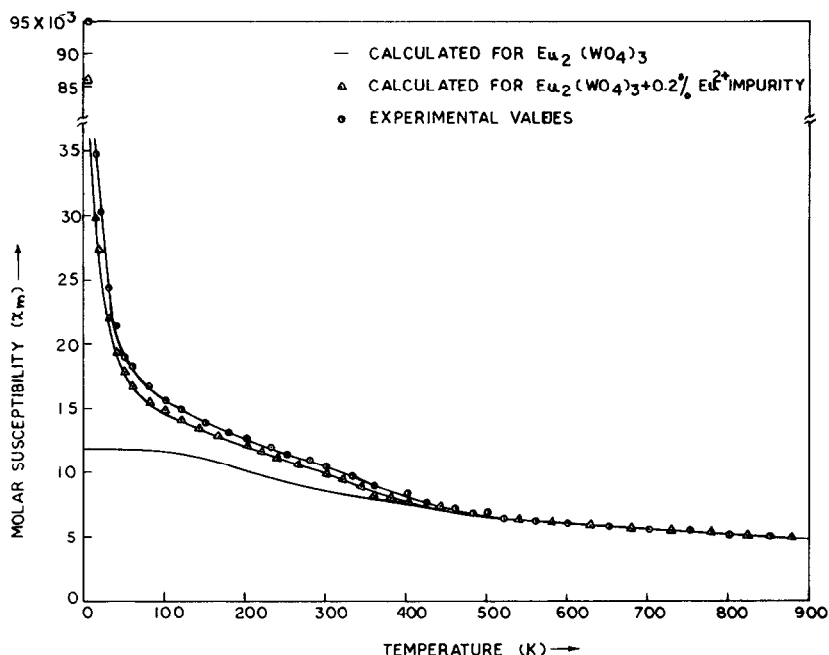
Fig. 3. Variation of the molar magnetic susceptibility (x_m) of $Eu_2(WO_4)_3$ powder vs. temperature.

Eu^{2+} ions. Taking 0.2% ions present in the solid, their contribution to the susceptibility at different temperature has been evaluated using the Curie law. Taking these contributions into account a corrected theoretical curve was obtained as marked by the triangles ($\triangle$) in fig. 3. It is seen that the agreement between this curve and the experimental curve is reasonably good. The discrepancies may be assigned to crystal-field and/or anisotropic exchange effects. Similar discrepancies have been observed in Eu_2O_3 by Huang and Van Vleck [13] and in EuF_3 by Kern et al. [14].

From fig. 2 it is seen that at high temperatures ($T > 300$ K) the values of χ_m are almost the same for the three crystallographic directions, but they differ considerably at low temperatures (fig. 1). Since impurity contents have a significant effect on the susceptibility values at low temperatures, the anisotropy appearing in fig. 1 is not very meaningful. When the contributions to the susceptibility due to impurities (0.2% Eu^{2+}) are subtracted, the corrected curves show the variations of χ_m with temperature for the three crystallographic directions. These curves are shown in fig. 4. It is seen from this figure that χ_{mb} increases as the temperature is lowered. This increase becomes much faster below about 80 K. On the other hand χ_{mc} and χ_{ma} decrease with decreasing temperature

below a temperature of 100 K and 80 K, respectively. χ_{ma} and χ_{mb} are almost equal above 150 K. But χ_{mc} differs from χ_{ma} and χ_{mb} up to about 450 K. It is well known that the anisotropy [15] in χ_m, in any solid may be due to (i) dipolar interaction between magnetic ions; (ii) anisotropic exchange interaction between dipolar ions; or (iii) crystal-fields acting on such ions. The second source of anisotropy is a combined effect of L–S coupling and exchange interaction [16, 17] and is particularly important for ferromagnetic metals. The magnetic exchange interactions between Eu^{3+} ions are probably very weak [18]. Even at liquid helium temperature it has been shown experimentally [19] that the susceptibility of Eu^{3+} ions in Eu_2O_3 is independent of their concentration, suggesting that exchange interactions give no net contribution to the susceptibility. The impurity ion Eu^{2+} is a spherically symmetric ion, so it does not lead to any anisotropic exchange and it will also not be affected by the crystal field. Dipolar interactions between rare-earth ions usually become of importance at temperatures lower than those of liquid helium only [19, 20]. These arguments suggest that sources (i) and (ii) listed above are too weak to give such large anisotropy.

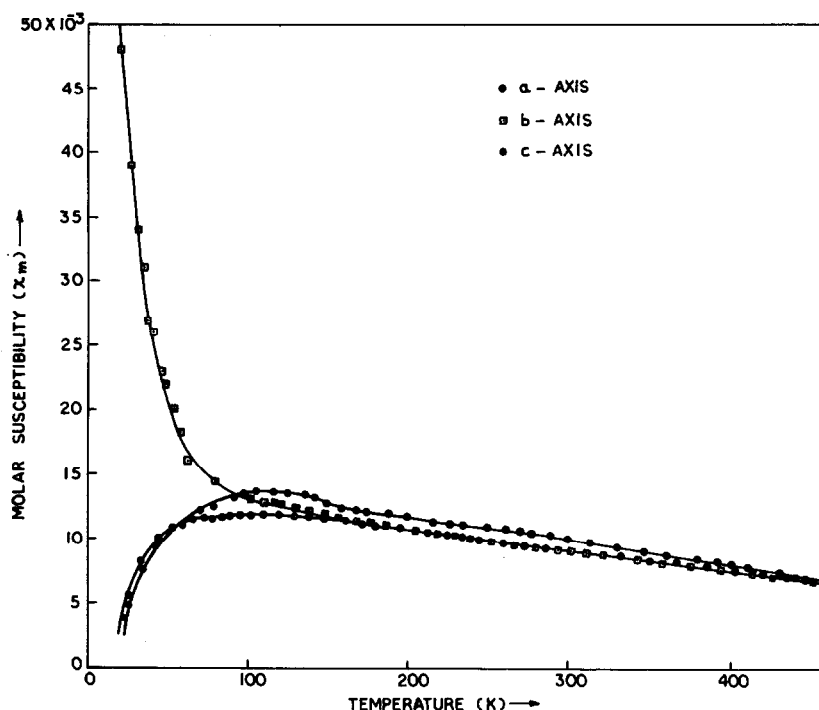Thus it seems that the crystal field alone is the

Fig. 4. Variation of the molar magnetic susceptibility (χ_m) (after the correction for a 0.2% Eu^{2+} impurity content) of Eu$_2$(WO$_4$)$_3$ single crystals vs. temperature.

prime source of anisotropy in χ_m. In rare-earth ions the 4f magnetic electrons are well buried inside the 5s and 5p orbitals and hence are not much affected by the crystal field. Numerical calculation shows, however, that the crystalline field even in cubic symmetry is larger than the multiplet width [20]. Various authors have shown that it leads to a Curie–Weiss law in many rare-earth solids [20, 21]. It is strong enough to give a paramagnetic Curie temperature of approx. 50 K and its effects become important below 140 K [18]. The anisotropy observed in this solid is actually large below this temperature. These arguments would lead to the conclusion that the crystal field is the prime source of anisotropy in this crystal.

Acknowledgements

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