Low Temperature Magnetic Susceptibility of $Sm_2(WO_4)_3$

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The magnetic susceptibility of powder samples of $Sm_2(WO_4)_3$ has been measured in the temperature range 4.2 to 300 K. At low temperatures the measured values disagree with those calculated for Sm^{3+}-ions using Van Vleck's theory. The high values below 100 K are assigned to magnetic exchange and dipol interactions. There might be magnetic ordering below 4.2 K. The effects of the crystal field and impurities have been shown to be unimportant.

The magnetic properties of samarium and europium ions are unique among the rare-earths[1]. They do not obey Hund's formula and the usual Curie Weiss law. The descrepancy between the theoretical and experimental values of the magnetic susceptibility is removed by inclusion of the second order Zeman effect[1]. Because of the unique behaviour of the Sm^{3+} ion and the magnetic ordering observed in some of its compounds[2, 3] the study of the magnetic susceptibility at low temperature of more of its compounds seems interesting and important. Such studies can give valuable information regarding magnetic ordering, phase transitions and exchange interactions. For the last few years we have been studying the transport and magnetic properties of rare earth tungstates[5–7]. This note reports our studies of the magnetic susceptibility of $Sm_2(WO_4)_3$ from 4.2 to 300 K. No such study exists in the literature till now.

Samarium tungstate is light yellowish in colour, has a density of 7.32 g cm^{-3} and a melting point between 1150 to 1220 °C[8]. It has a monoclinic unit cell ($a = 7.711$ Å, $b = 11.504$ Å, $c = 11.468$ Å and $\beta = 109.8°$) and belongs to the $C_2(C_{6h})$ space group with four molecules per unit cell. The lattice can also be looked at as pseudo-orthorhombic with the unit cell dimensions $a = 7.68$, $b = 11.504$ and $c = 21.41$ Å. The unit cell in this case contains 8 molecules[8, 9].

For of the preparation of $Sm_2(WO_4)$ we have used the method reported by Brixner and Sleight[9]. Our starting materials were Sm_2O_3 (99.9%, Fluka AG, Switzerland) and analytical grade WO_3 (99.9% E. Merk, Germany), both dried at 900 K for a few hours. The structure of the product was checked by X-ray powder photography. The melting point was in the range mentioned above. No mass spectrographic studies were done. We expect the original impurities (0.1%) to exist as oxides or tungstates.

The magnetic susceptibility was measured using a Vibration Sample Magnetometer. The sample vibrates perpendicular to a constant and homogeneous magnetic field and the a.c. signal induced in a pair of pick up coils is measured and compared with that from a nickel standard sample. The magnetization of the powder sample (1 ∼ 50 mg) could continuously be recorded as a function of temperature (4.2 to 300 K) and external field strength (0 to 10 kOe).

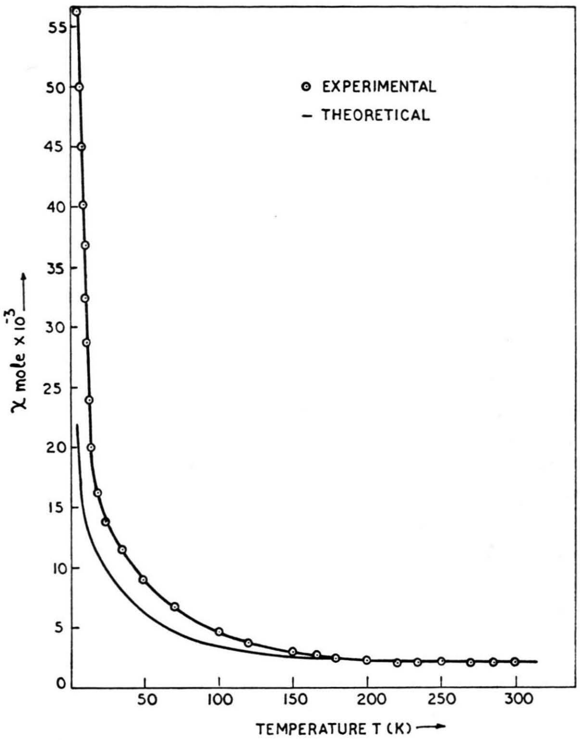

Fig. 1. The variation of the magnetic susceptibility (per gram mole) with temperature of a powder specimen of $Sm_2(WO_4)_3$. Theoretical curve for free Sm^{3+}-ions.

The results are shown in Figure 1. The main contribution to the susceptibility comes from the Sm^{3+} ions. It is well known that the energy separation between the consecutive multiple levels of Sm^{3+} for different values of J is very small compared to kT. The applied magnetic field can admix the ground state ($J = 5/2$) to multiples with higher values of J. Hence, in order to calculate the magnetic susceptibility of the Sm^{3+} ion one has to take into account the contribution of higher states[3]. Van Vleck (1932) was the first to point this out and has

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given the formula

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

where E_J is the energy and χ_J the susceptibility for the J^{th} multiple level.

The susceptibility of Sm^{3+} ions has been evaluated by various workers [4–6] assuming a simple form of spin-orbit interaction. The result of such calculations, taking the number of Sm^{3+} ions to be that in a gram mole of $\text{Sm}_2(\text{WO}_4)_3$, is shown in Figure 1. The theoretical susceptibility of Sm^{3+} decreases quite rapidly with increasing temperature, goes through a minimum and then starts increasing again. This behaviour of Sm^{3+} is at variance with the Curie-Weiss law in which the susceptibility continuously decreases with temperature.

As evident from Fig. 1 our observed magnetic susceptibilities are larger than the theoretical ones, especially at low temperatures. The difference between the experimental and theoretical susceptibilities indicates a slight ordering of magnetic dipoles at low temperatures, giving a possible antiferro- and ferromagnetic ordering between sublattice and intralattice [13] ions, respectively. The difference in the number of dipoles at unquivalent sites may lead to a weak ferromagnetism [13]. This ordering can be verified only by neutron diffraction experiments for which we have no facility. However, it may be pointed out that such an ordering is expected only below 4.2 K. It is well known [14] that the simple dipole-dipole interaction is strong enough to align the dipoles below 1 K but not so at higher temperatures. The weak ferromagnetism arising, therefore, can not be attributed completely to dipol interactions.

An other possible reason for the increase in the susceptibility are paramagnetic impurity ions with a high effective number of Bohr magnetons. The maximum amount of impurities which can be present is 0.1% according to the stated purity of the substances used in the preparation of the $\text{Sm}_2(\text{WO}_4)_3$. The common impurities expected are the other rare-earth ions. It can be verified that their contribution would be too low to explain our experimental results at low temperatures.

Besides impurities, the crystal field can effect the χ values [14]. The effects of the crystal field are, (i) to break the coupling of the $L-S$ vector so that the states are no longer specified by their J values (ii) to quench the orbital angular momentum so that the spin alone contributes to the susceptibility. At lowest temperatures only the ground state is expected to be populated. The ground state of Sm^{3+} is $^6\text{H}_{5/2}$ giving $L=0$. Thus the crystal field effect on this ion is expected to be very small. In general rare-earth ions are little affected by the crystal field [14] and it's effect is to decrease the χ values [14, 15]. Thus also the crystal field cant contribute to the large χ values.

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[1] J. H. Van Vleck, The Theory of Electric and Magnetic Susceptibilities, Oxford University Press, Oxford 1932, pp. 226.

[2] A. Frank, Phys. Rev. **39**, 119 [1932].

[3] G. Busch, J. Appl. Phys. **38**, 1386 [1967].

[4] M. Eibschutz, G. Gorodetsky, S. Shtrikman, and D. Treves, J. Appl. Phys. **35**, 1071 [1964].

[5] H. B. Lal, N. Dar, and Ashok Kumar, J. Phys. C: Solid State Phys. **7**, 4335 [1974].

[6] H. B. Lal, N. Dar, and A. Kumar, J. Phys. C: Solid State Phys. **8**, 2745 [1975].

[7] H. B. Lal, A. Kumar, and N. Dar, Curr. Science **43**, 305 [1974].

[8] K. Nassau, H. J. Levinstein, and G. M. Loiacono, J. Phys. Chem. Solids **26**, 1805 [1965].

[9] L. H. Brixner and A. W. Sleight, Mat. Res. Bull. **8**, 1269 [1973].

[10] S. Foner, Rev. Sci. Instrum. **30**, 548 [1959].

[11] A. S. B. Romonov and N. M. Kreines, Sov. Phys. JETP **2**, 659 [1956].

[12] R. M. Bozorth and J. H. Van Vleck, Phys. Rev. **118**, 1493 [1960].

[13] J. B. Goodenough, Magnetism and Chemical Bond, John Wiley, New York 1965, pp. 75.

[14] D. H. Martin, Magnetism in Solids, Ileffe Book Limited, London 1967.

[15] J. F. Thomas and M. J. Seinko, J. Chem. Phys. **61**, 3920 [1974].