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Unusual magnetic behaviour of heavy rare earth vanadates at higher temperature

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Mixed oxides of rare earth and iron group elements are well known for their wide ranging physical properties. Among them vanadates of rare earth elements form a group of compounds revealing interesting structural and magnetic transformations at low temperature [1]. Recently we have reported magnetic susceptibility studies on $GdVO_4$ [2] and light rare earth vanadates [3] (RVO_4, where R stands for La, Ce, Pr, Nd, Sm and Eu). In $GdVO_4$ we observed ferromagnetic type behaviour, whereas unusual behaviour, in the form of peaks and drops in the magnetic susceptibility against temperature curve, has been observed for light rare earth vanadates. These results have been explained as due to thermal generation and exchange interaction of magnetic V^{4+} ions. Prompted by these results we have further investigated the magnetic behaviour of other RVO_4 to complete the series. This paper reports on the study of the magnetic susceptibility of heavy rare earth vanadates [RVO_4, where R stands for Gd, Tb, Dy, Ho, Er and Yb] in the temperature range 295 to 925 K. Gd has been included for the sake of comparison; Tm and Lu could not be included because we could not procure the oxides of these materials.

All heavy rare earth vanadates were prepared using respective R_2O_3 and V_2O_5. All R_2O_3, with a stated purity of 99.99%, were procured from M/S Rare-Earth Product, England; whereas V_2O_5, with stated purity of 99.99%, was obtained from M/S Bonds, India. These compounds, except for drying around 400 K for a few hours, were used as-received in the preparation of the vanadates. The oxides were mixed in stoichiometric amounts, pelletized and fired repeatedly in air around a temperature of 1500 K. The compounds were formed and none of the oxides remained unreacted after two successive firings. The magnetic susceptibility of the starting materials, as well as of the prepared compounds, was measured at different temperatures and fields using Faraday's method. Experimental details are described elsewhere [4].

The magnetic susceptibility of the starting materials was measured in the temperature range 295 to 900 K at low fields. V_2O_5 was found to be diamagnetic in the entire temperature range, where magnetic susceptibility values, Curie constants and paramagnetic Curie temperatures of their oxides agreed fairly well with the data reported in the literature [5]. This ruled out any significant para- or ferromagnetic impurity in the starting materials. The variation of molar magnetic susceptibility, χ_M, with absolute temperature, T, for Gd, Tb, and Dy vanadates are shown in Figs. 1a, b and c respectively. The same plot is shown for Ho, Er and Yb vanadates in Figs. 2a, b and c. Figs. 3a, b and

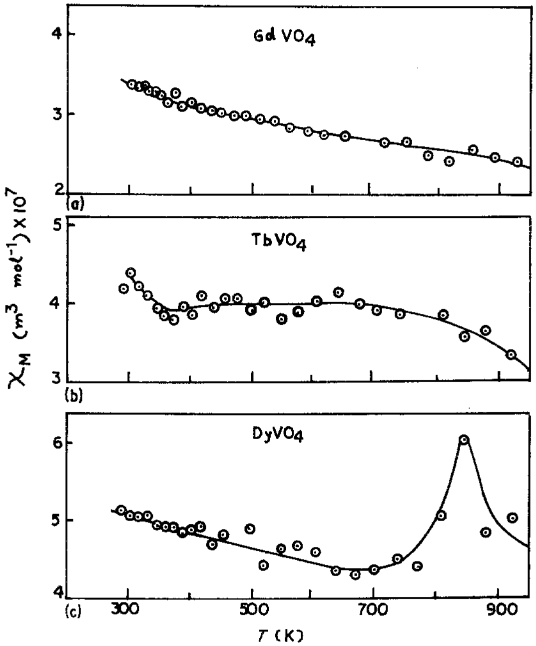

Figure 1 Variation of molar magnetic susceptibility, χ_M, with absolute temperature, T, for (a) $GdVO_4$, (b) $TbVO_4$ and (c) $DyVO_4$.

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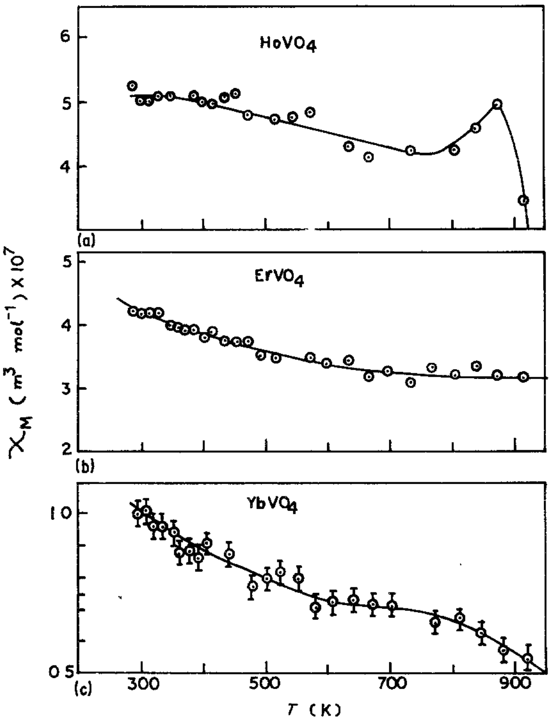

Figure 2 Variation of molar magnetic susceptibility, χ_M, with absolute temperature, T, for (a) $HoVO_4$, (b) $ErVO_4$ and (c) $YbVO_4$.

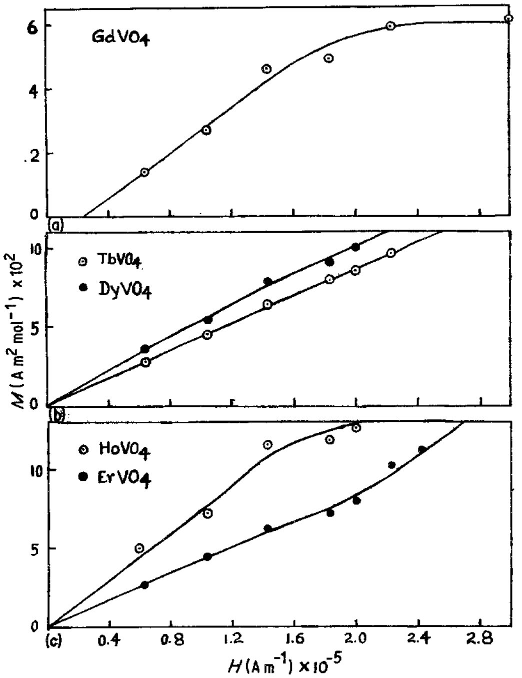

Figure 3 Variation of magnetization, M, with magnetic field, H, for (a) $GdVO_4$, (b) $TbVO_4$ and $DyVO_4$ and (c) $HoVO_4$ and $ErVO_4$.

c show plots of magnetization, M, with applied magnetic field, H at 295 K for Gd, Dy and Tb and Ho and Er vanadates respectively.

The molar magnetic susceptibility variations with temperature for Gd and Er vanadates are similar. Here molar magnetic susceptibility decreases continuously with temperature. Almost similar behaviour is observed in the case of $YbVO_4$. However, here the tendency appears for a flat maximum around 775 K. In the case of $TbVO_4$, after a linear decrease between 295 to 400 K, χ_M remains almost constant up to 675 K, then decreases with increase in T. Very similar behaviour is witnessed in Dy and Ho vanadates. For both these compounds χ_M decreases systematically up to 700 K, then increases and shows a peak around 845 K for Dy and 875 K for Ho vanadates. At room temperature the magnetization against magnetic field plot for the vanadates studied is shown in Figs. 3a, b and c. All these vanadates except that of Yb are pulled towards the pole pieces when the field is increased. Therefore measurement could not be performed at higher magnification fields. The nonlinearity of M against H curve is apparent very clearly in the case of Gd. In other vanadates it appears to be nonlinear.

If all the vanadates are taken as ionic compounds, we except that in these solids the rare earth ions will exist in the trivalent state, vanadium ions in the pentavalent state and oxygen ions in the divalent state. Since the latter two ions, namely V^{5+} and O^{2-}, are nonmagnetic and give only a small diamagnetic contribution to χ_M, the major contribution to χ_M in RVO_4 should come from the rare earth ion. The exchange interaction between rare earth ions is small and they become ordered, overcoming thermal energy only at very low temperature [6]. Above room temperature contribution to susceptibility for all rare earth ions (Gd to Yb) is of the form $\chi_M = C(T-\theta)^{-1}$, where C is the Curie constant for the ion and θ is the paramagnetic Curie temperature. Thus we expect that the rare earth vanadates studied should have smooth variation of χ_M with T. This is, however, contrary to the experimental results obtained, wherein some cases we obtain peaks and drops in χ_M values at specific temperatures. As we have mentioned in earlier papers [2, 3], the VO_4 tetrahedra in RVO_4 are distorted and thus the V–O linkage may not be perfectly ionic but partially covalent. The vanadium ion, then, is expected to exist in an intermediate ionic state between V^{5+} and V^{4+} and hence may contribute to susceptibility. The covalency may increase with temperature. It is also possible that an electron from the O^{2-}, 2p state of the oxygen ion is excited and reaches the V^{5+}: 3d shell of a neighbouring V^{5+} ion, thereby coverting it into a V^{4+} ion. In any case there is a fair possibility of the existence of V^{4+} ions in these vanadates at room temperature and their number may increase exponentially with temperature. These ions will contribute to χ_M significantly. Since the magnetic contribution in V^{4+} ions is due to 3d electrons, which are in the outermost orbit of the ion, they have a sufficient chance of overlapping with neighbouring ions and interacting with the crystal field. Therefore, when their number becomes large, they may interact magnetically among themselves and contribute significantly towards magnetic susceptibility. It is not possible to predict the form of the interaction and tendency in these ions in the different vanadates, but we have already concluded that in Gd they interact to produce ferromagnetic ordering. The peaks observed in Dy and Ho vanadates may be explained if one assumes antiferromagnetic ordering of thermally generated V^{4+} ions in these solids. When their number is large they may order to give a peak in the χ_M against T plot at a specific temperature, say T_0. Both below and above T_0, they may again become disordered: at the lower temperature side because of their lower number (larger distance), and at higher temperature side because of the higher value of thermal energy. In general, we may conclude that unusual variations of χ_M with T in RVO_4 are due to a thermally generated exponential increase in the number of V^{4+} ions in these solids.

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