Spin-state equilibria in YbCoO_3

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Abstract. The relative properties of high spin and low spin Co^{3+} in HoCoO_3 , ErCoO_3 and LuCoO_3 are about 1 : 1 above a characteristic temperature. YbCoO_3 seems to show a similar behaviour with no evidence of electron transfer between the high spin and low spin states.

Keywords. Spin-state equilibria ; electron transfer ; characteristic temperature ; rare-earth cobaltites.

1. Introduction

Detailed studies on transport and magnetic properties have been carried on a number of rare earth cobaltites of the formula LnCoO_3 . These studies show the dependence of spin-state equilibria on the size of the rare-earth ion. In the lighter rare earth cobaltites (Raccah and Goodenough 1967 ; Bhide *et al* 1971 ; Jadhao *et al* 1976) such as LaCoO_3 , electron transfer from the high spin Co^{3+} ($t_{2g}^4 e_g^2$) to low spin Co^{III} ($t_{2g}^6 e_g^0$) takes place at high temperature above a characteristic temperature, T_i , giving rise to Co^{II} ($t_{2g}^6 e_g^1$) and Co^{IV} ($t_{2g}^4 e_g^1$) states. Such electron transfer provides the mechanism of conduction in the lighter rare earth cobaltites. However, in case of the heavier rare-earth cobaltites (Jadhao *et al* 1975 ; Bhide *et al* 1973 ; Bahadur 1976) such as HoCoO_3 , ErCoO_3 and LuCoO_3 , Co^{3+} and Co^{III} get equally populated above T_i and there is no evidence of electron transfer in these cobaltites. This interesting behaviour of cobalt spin-states has been attributed to the effect of the size of the rare earth ion, the smaller ions being associated with acidity. We have investigated the spin-state equilibria in YbCoO_3 which confirm this conclusion based on earlier studies.

2. Experimental

YbCoO_3 was prepared by the thermal decomposition of $\text{YbCo}(\text{CN})_6 \cdot 6\text{H}_2\text{O}$ which was prepared by the reaction of ytterbium chloride with potassium cobalti-

Figure 1. Plot of χ_g^{-1} against temperature of YbCoO_3

Figure 2. Plot of $\chi_g T$ against temperature for YbCoO_3

cyanide. $\text{YbCo}(\text{CN})_6 \cdot 6\text{H}_2\text{O}$ was decomposed at 1000 K for five hours to give YbCoO_3 . Thermogravimetric analysis shows that the cobaltcyanide decomposes to the cobaltite below 900 K which are stable up to at least 1200 K. X-ray diffraction data of YbCoO_3 could be indexed on the basis of an orthorhombic structure with $a = 5.080 \text{ \AA}$, $b = 4.422 \text{ \AA}$ and $c = 7.318 \text{ \AA}$.

3. Results and discussion

The inverse magnetic susceptibility of YbCoO_3 is plotted against temperature in figure 1. This plot does not show an obvious plateau like LaCoO_3 . However, there is a change in slope around 550 K. Effective magnetic moment below and above this temperature are 3.85 and 3.96 μ_B respectively. These results indicate that the effective Bohr magneton per cobalt ion is slightly different in the two regions.

Since, $\chi_g T$ is directly related to spin-state population (Bhide *et al* 1971, 1973), we have plotted $\chi_g T$ against T in figure 2. The plot shows a marked increase beyond 550 K, but remains essentially constant beyond 750 K. Below 550 K, also $\chi_g T$ is essentially constant. This behaviour is typical of all other heavier rare earth cobaltites like HoCoO_3 and ErCoO_3 . It appears that in YbCoO_3 , the ratio of $\text{Co}^{3+}/\text{Co}^{\text{III}}$ remains roughly the same but less than 1 below 550 K. This ratio changes between 550-750 K; and above 750 K, the two spin-states appear to be equally populated. The constancy of $\chi_g T$ versus T at high temperatures also indicates that there is no electron transfer. The absence of electron transfer between Co^{3+} and Co^{III} is also evident from the high electrical resistivity of YbCoO_3 at room temperature. These results show that the behaviour of YbCoO_3 is similar to that of other heavier rare earth cobaltites and confirm that the size of the rare-earth ion play an important role in determining spin-states equilibria in the cobaltites.

References

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