Magnetic Properties of Zn Substituted Co-Ti Spinels

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The magnetic properties of cobalt titanate, Co_2TiO_4, and zinc substituted cobalt titanate, $Co_{2-x}Zn_xTiO_4$ (x=0.2~1.2), have been investigated between 1.6°K and 400°K. These materials have the spinel structure and become ferrimagnetic at low temperatures. $Co_{1.8}Zn_{0.2}TiO_4$ has a ferrimagnetic Curie temperature 45°K, and its spontaneous magnetic moment has a maximum at 35°K. Just below 20°K a magnetic viscosity effect is observed. At liquid helium temperature magnetic behavior depends largely on the condition of cooling. If the sample is cooled in a magnetic field of a few kilo oersteds, its hysteresis loop shifts along the positive magnetization axis while that of Co_2TiO_4 shifts along the negative one. The unidirectional torque is also observed at liquid helium temperature. Small values of the maximum spontaneous magnetic moment, 0.04 μ_B for Co_2TiO_4 and 0.1 μ_B for $Co_{1.8}Zn_{0.2}TiO_4$, suggest that these materials may have a canted spin arrangement.

1. Introduction

Cobalt titanate with formula Co_2TiO_4 is reported by Romeijn[1] to be an inverse spinel, $Co(CoTi)O_4$. However, the magnetic property of this material has not yet been reported.

We have investigated the magnetic properties of Co_2TiO_4 and zinc substituted cobalt titanate, $Co_{2-x}Zn_xTiO_4$. Since Zn^{2+} ions substitute for Co^{2+} ions in tetrahedral sites, a ferrimagnetism will be expected in zinc substituted cobalt titanate. Furthermore, since the orbital contribution to the magnetic moment of Co^{2+} in octahedral sites is larger than that of tetrahedral sites, a net moment may appear in Co_2TiO_4. Our measurements of magnetization and of magnetic torque show that these compounds possess a ferrimagnetic arrangement. Some unusual magnetic behavior, such as displaced hysteresis loop, unidirectional torque etc., have been found at low temperatures.

2. Experimental Results and Discussion

Titanates with formula $Co_{2-x}Zn_xTiO_4$ were prepared by usual ceramic techniques. The values of x are 0.0~1.2 at intervals of 0.2. X-ray measurements confirmed them to have a spinel structure. A single crystal of Co_2TiO_4 was grown from melt by Stockbarger-Bridgman method. Details of sample preparation and experimental procedures are described in other paper[2]. Preliminary paramagnetic susceptibility measurements of these compounds are made between 77°K and 400°K. The asymptotic Curie temperature of Co_2TiO_4 is −80°K and the effective number of Bohr magneton is 4.7, while those of $Co_{0.8}Zn_{1.2}TiO_4$ are −20°K and 5.4 respectively.

The magnetization versus temperature curve of pure cobalt titanate is shown in Fig. 1 and that of $Co_{1.8}Zn_{0.2}TiO_4$ as an ex-

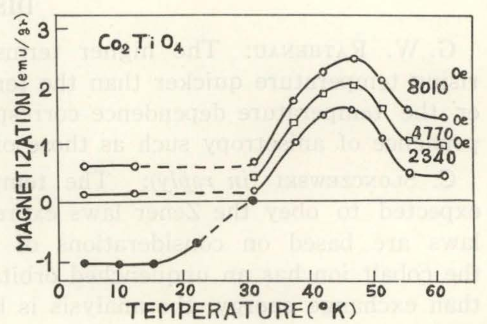

Fig. 1. Magnetization versus temperature curves of Co_2TiO_4. Black points are the negative remanences of the displaced hysteresis loops.

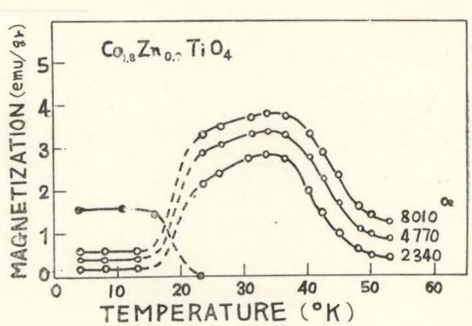

Fig. 2. Magnetization versus temperature curves of $Co_{1.8}Zn_{0.2}TiO_4$. Black points are the positive remanences of the displaced hysteresis loops.

ample of zinc substituted cobalt titanate is shown in Fig. 2.

The ferrimagnetic Curie temperature of $Co_{1.8}Zn_{0.2}TiO_4$ is 45°K. On lowering the temperature, the spontaneous magnetization rises to a maximum at 35°K, then decreases slowly at first, and rapidly decreases to nearly zero at 20°K. However, if this sample was cooled in a magnetic field to lower temperatures than 20°K, anomalous magnetic behavior was observed. Typical hysteresis loops of this sample are shown in Fig. 3. In the temperature range between 45°K and 20°K, hysteresis loops are symmetrical about the origin. At liquid helium temperature, hysteresis loop is also symmetrical when the sample is cooled in the absence of any applied magnetic field, though the magnetization is small.

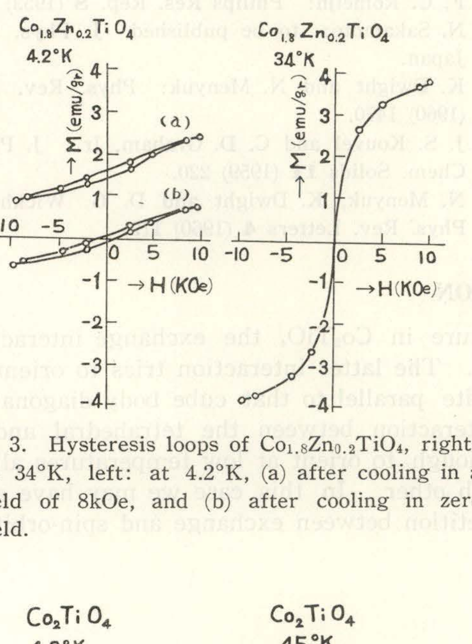

Fig. 3. Hysteresis loops of $Co_{1.8}Zn_{0.2}TiO_4$, right: at 34°K, left: at 4.2°K, (a) after cooling in a field of 8kOe, and (b) after cooling in zero field.

However, it shifts to the positive side along the magnetization axis when the sample is cooled in a magnetic field of 8 kOe through 20°K. The polarity of the field axis is defined by taking the field applied during cooling as positive. Values of positive remanence below 20°K are plotted in Fig. 2 as black points. Hysteresis loops of Co_2TiO_4 are shown in Fig. 4. The general feature is similar to $Co_{1.8}Zn_{0.2}TiO_4$. However there is one important difference. The sign of the displaced hysteresis loop is negative in contrast to that of zinc substituted samples.

Torque measurements on a single crystal of Co_2TiO_4 at 4.2°K confirmed this negative displacement. When the sample is cooled in the absence of any applied field, the torque

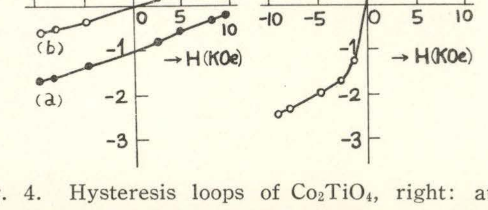

Fig. 4. Hysteresis loops of Co_2TiO_4, right: at 45°K, left: at 4.2°K, (a) after cooling in a field of 8kOe, and (b) after cooling in zero field.

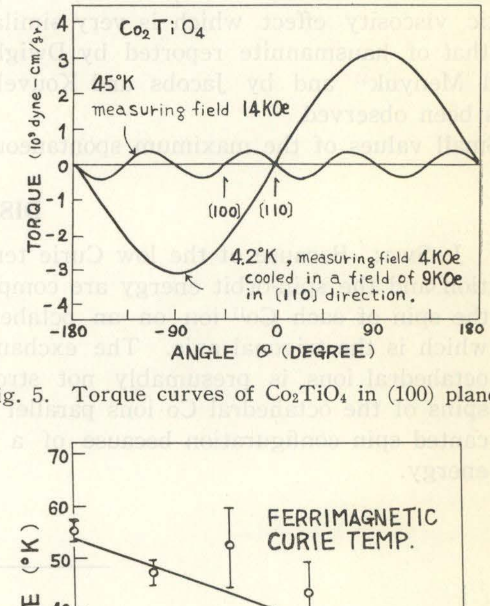

Fig. 5. Torque curves of Co_2TiO_4 in (100) plane.

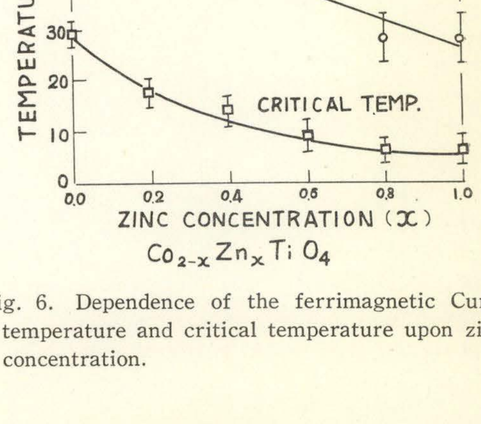

Fig. 6. Dependence of the ferrimagnetic Curie temperature and critical temperature upon zinc concentration.

is very small, but when it is cooled in a magnetic field of 9 kOe a $\sin\theta$ variation of torque, unidirectional torque, is observed as shown in Fig. 5, where θ is the angle between the direction of measuring field and that of applied field during cooling. The easy direction of the torque is opposite to the direction of the field during cooling.

Torque at 45°K in (100) plane has a fourfold symmetry as should be in a cubic crystal. Its easy axis is along ⟨110⟩ direction. The anisotropy constant K_1 is estimated to be about 4000 erg/c.c..

The dependence of the ferrimagnetic Curie temperature and the critical temperature upon zinc concentration are shown in Fig. 6. The critical temperature is defined as the temperature where the negative or positive remanence, or the unidirectional torque, disappear on warming.

Just below the critical temperature, a magnetic viscosity effect which is very similar to that of hausmannite reported by Dwight and Menyuk[3] and by Jacobs and Kouvel[4] has been observed.

Small values of the maximum spontaneous magnetic moment, 0.04 μ_B for Co_2TiO_4 and 0.1 μ_B for $Co_{1.8}Zn_{0.2}TiO_4$, suggest that these materials may have a canted spin arrangement. So it has been recently reported[3),4),5)] that many other materials with canted spins exhibit anomalous behavior at low temperatures, unusual magnetic behavior of both Co_2TiO_4 and $Co_{2-x}Zn_xTiO_4$ will be associated with a canted spin structure.

Acknowledgements

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References

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DISCUSSION

J. SMIT: Because of the low Curie temperature in Co_2TiO_4 the exchange interaction and the spin-orbit energy are comparable. The latter interaction tries to orient the spin of each Co^{II} ion on an octahedral site parallel to that cube body diagonal which is the trigonal axis. The exchange interaction between the tetrahedral and octahedral ions is presumably not strong enough to orient at low temperatures all spins of the octahedral Co ions parallel to each other. In this case we may have a canted spin configuration because of a competition between exchange and spin-orbit energy.