MAGNETIZATION REVERSAL AND ASYMMETRY IN COBALT VANADATE (IV)*

N. Menyuk, K. Dwight, and D. G. Wickham
Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts
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A study of the magnetic properties of a powdered sample of cobalt vanadate (IV), Co_2VO_4, has disclosed the presence of a number of unusual effects. X-ray measurements[1] taken on this sample show it to be a single-phase spinel, with an indication of the presence of a small amount ($\approx 1\%$) CoO. Paramagnetic measurements were made between 250°K and 450°K in order to determine the oxidation state of the cations. Since Co^{2+} cations have different moments on octahedral (B) and tetrahedral (A) sites,[2] we were also able to determine that cobalt vanadate (IV) forms the inverse spinel $Co^{2+}[Co^{2+}V^{4+}]O_4$.

This material has a ferrimagnetic Curie temperature $T_C = 158$°K. On decreasing the temperature, the spontaneous magnetic moment rises rapidly to a maximum at $T = 139$°K, then decreases to a zero net moment at a compensation temperature $\theta_C = 70$°K. On taking a magnetization curve in the presence of a small field ($H = 700$ oersteds), the net magnetization below 70°K is opposite to the direction of the applied field, as shown in Fig. 1. Compensation points of this type have been observed in ferrimagnetic systems since they were first predicted by Néel[3]; however, the low value of θ_C/T_C obtained in Co_2VO_4 is more typical of garnets[4] than of other spinels.[5]

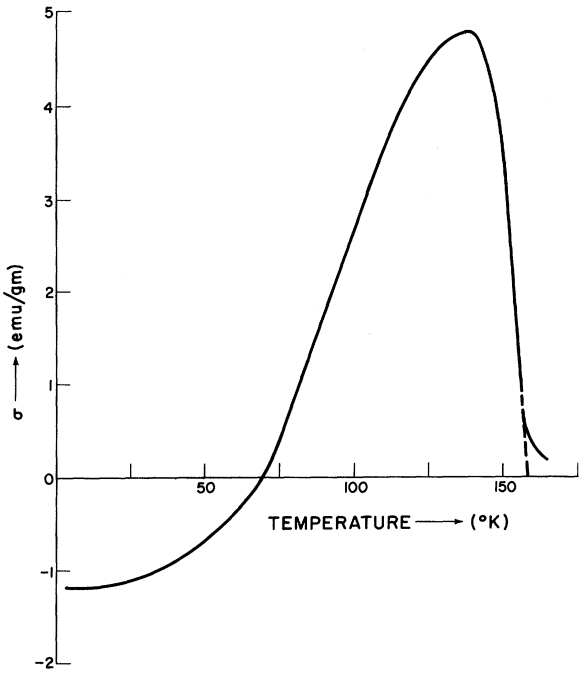

FIG. 1. Temperature dependence of magnetization of Co_2VO_4 in an external field of 700 oe.

The dependence of magnetization upon fields applied in the same direction as that applied during cooling was investigated at 4.2°K. The resultant curve, which shows a large asymmetry along the magnetization axis, is given in Fig. 2. If the sample is then rotated approximately 90°, a symmetrical hysteresis loop is obtained which is qualitatively similar in shape to the first curve. Furthermore, on returning the sample to its original position relative to the field, the original asymmetry is restored. Thus 11 000 oersteds at 4.2°K are unable to destroy the memory of the field direction during cooling.

Asymmetrical hysteresis loops are as uncommon as compensation points, and in no previous case have both phenomena been reported in the same substance. Exchange interactions observed by Meiklejohn and Bean[6] between cobalt and antiferromagnetic cobaltous oxide give rise to a large asymmetry along the field direction, in marked contrast with our results. This would appear to eliminate the small amount of cobaltous oxide impurity in our sample as the source of this effect.

Reports of materials exhibiting asymmetry along the magnetization axis have been limited

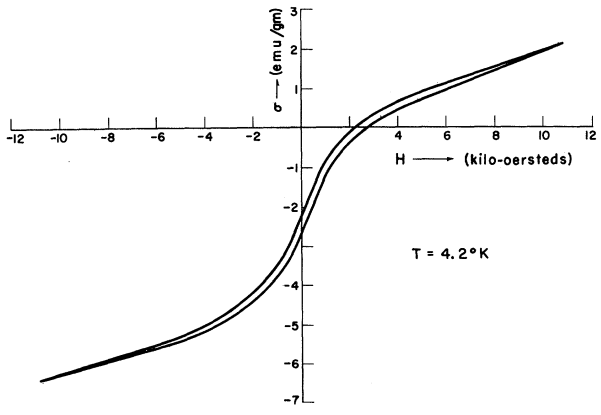

FIG. 2. Hysteresis loop of Co_2VO_4 at 4.2°K. The polarity of the field axis is defined by taking the field applied during cooling as positive.

to a small effect in antiferromagnetic UMn_2,[7] and to a two-phase magnetic system containing α-Fe_2O_3 and $LaFeO_3$.[8] In the latter case the hysteresis loop was explained as a symmetrical α-Fe_2O_3 loop superimposed upon a very hard magnetization in one direction. This explanation cannot be applied indiscriminately to our sample because it is essentially a single-phase material.

However, $Co^{2+}[Co^{2+}V^{4+}]O_4$ represents a complicated magnetic system. Magnetic interactions of A-site cations with B-site cations (A-B interactions) and of B-site cations amongst themselves (B-B interactions) give rise to five distinct interactions.[9,10] These interactions make it possible to obtain the multiple magnetic effects required to understand the experimental results. The simplified discussion given below indicates the manner in which these interactions can bring about the observed phenomena. In cobalt vanadate (IV) the Co^{2+}-O^{2-}-Co^{2+}, A-B interaction is the strongest single interaction[9] and will give rise to a net magnetic moment whether or not a canted spin arrangement[2,11-13] of the cobalt ions exists. In addition, a weaker A-B, Co^{2+}-O^{2-}-V^{4+} interaction exists as well as a direct B-B, V^{4+}-V^{4+} interaction.[10] If these latter two interactions are of comparable magnitude, the vanadium ions will have a canted spin arrangement with a net magnetic moment. This vanadium moment, with a net effect antiparallel to that of the cobalt ions but with a different temperature dependence, could give rise to a compensation effect.

In order to explain the hysteresis loop behavior at 4.2°K it is necessary that the vanadium and cobalt cations behave differently under the action of an applied field. In view of the high anisotropy and magnetic hardness of cobalt in spinel lattices,[14,15] it is reasonable to assume that an applied field of 11 000 oersteds is incapable of reversing the spins of the cobalt ions at 4.2°K after they have been set by cooling through the Curie point in an external field. The variation of magnetization at low fields is then due to a rotation of the vanadium ion spins relative to the cobalt, while the high-field magnetization variation can be caused either by the anisotropy or by a canted spin arrangement of the cobalt ions.

An additional hysteresis loop taken at 120°K was symmetric. The abruptness of the magnetization change with applied field at this temperature indicated that the low-field effect ($H \leq 3000$ oe) present at 4.2°K is essentially absent. This is in general accord with the assumption that the vanadium ion interactions become more important at lower temperatures. The explanation given above ignores the effects of Co^{2+}-V^{4+} and Co^{2+}-Co^{2+}, B-B interactions as well as the effects of the statistical distribution of B-site cations. However, despite the simplifications, the above description should be illustrative of the true behavior of the sample. A detailed understanding of the behavior requires more accurate knowledge of the various magnetic interactions than is presently available. This information will be obtained by substitution of nonmagnetic cations for vanadium and cobalt and by a neutron diffraction study.

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