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Magnetic Studies on Fe_2MoO_4

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Magnetization measurements, neutron diffraction studies, and Mössbauer spectroscopy have been used to investigate the unusual magnetic properties of the inverse spinel oxide Fe_2MoO_4. It is concluded that the Mo^{4+} ion is not low-spin ($S = 0$), as had previously been postulated, but has two unpaired electrons which play a crucial role in the overall magnetic behavior of the compound. The small moment of $0.2\mu_B$ per formula and thermoremanent behavior below 50°K are thought to be due to a strong B–B interaction, comparable to the A–B interaction, resulting in a breakdown of the Néel model.

Introduction

The inverse spinel oxide Fe_2MoO_4 has several unusual magnetic properties. Not only does it have a "compensation temperature" at which the magnetic moment passes through zero (*1*), but the experimentally obtained magnetic moment, about $0.2\mu_B$, differs from that calculated on the basis of its formula whatever stoichiometrically permissible combination of Fe^{2+}, Fe^{3+}, Mo^{2+}, Mo^{3+}, and Mo^{4+} is chosen. In fact, numerous lines of evidence indicate that the compound is properly formulated as $Fe_2^{2+}Mo^{4+}O_4$ with half the Fe^{2+} on tetrahedral (A) sites and the rest of the Fe^{2+} together with the Mo^{4+} distributed on the octahedral (B) sites. Abe et al. (*2*) interpreted the data by assuming a zero moment for Mo^{4+} ($4d^2$) and perhaps a slightly canted antiferromagnetic coupling of the two Fe^{2+} ($3d^6$) moments. Although it is true that the 4*d* transition elements tend to show low-spin behavior in their compounds, both Mo^{3+} and Mo^{4+} have been found to behave magnetically like high-spin 3*d* transition elements (*3*, *4*). For example, the neutron diffraction and magnetization measurements of the halides of Mo^{3+} and Mo^{4+} show that there are 3 and 2 free spins, respectively. On the basis of 2 unpaired electrons for Mo^{4+}, the net moment for the inverse spinel Fe_2MoO_4 should be $2\mu_B$, assuming a strictly collinear arrangement:

$$Fe^{2+}[Fe^{2+}Mo^{4+}]O_4$$

$$4\mu_B\downarrow[4\mu_B\uparrow\ 2\mu_B\uparrow].$$

An alternative interpretation of the small observed magnetic moment ($0.2\mu_B$) would then be based on the noncollinear alignment of the Mo^{4+} spins in addition to the slight canting of the Fe^{2+} moments. To determine whether the molybdenum is in the high-spin or low-spin state we have made a detailed study of the magnetization, neutron diffraction, and Mössbauer spectrum of this compound. The results indicate that Mo^{4+} is indeed in the high-spin state, rather than low-spin as previously assumed (*2*), and also reveal some most interesting thermal behavior of this compound in a magnetic field.

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Experimental

Fe_2MoO_4 was prepared by heating the reduced oxides of Fe_2O_3 and MoO_3 in an atmosphere of CO_2/H_2 (1:1 by volume) at 1140°C for about 40 hr. The sample was cooled to 600°C at a rate of 100°C/hr maintaining the same reducing atmosphere, and then quenched to room temperature. Great care was taken to quench the sample in the reducing atmosphere because Fe_2MoO_4 readily reacts with air at elevated temperatures to give Fe_2O_3 and MoO_3 again.

The samples were checked by both X-ray and Mössbauer spectroscopy and no Fe_2O_3 was detected. The compound was indexed as a cubic spinel with $a = 850.6$ pm. Unlike Abe et al., we did not anneal our samples as we found that, although there was no detectable difference in the chemical analysis of annealed and unannealed samples, there was a difference in their magnetic behavior, i.e., the compensation temperature was lowered by annealing. This is probably due to a slight nonstoichiometry introduced as a result of oxygen deficiency in the samples annealed in a reducing atmosphere.

The magnetization measurements were carried out in a vibrating sample magnetometer, modified from that used by Foner (*5*), using a helium gas flow cryostat (*6*).

The neutron diffraction measurements on the powdered samples were done on Curran at UKAEA, Harwell, using a wavelength of 137.2 pm.

The Mössbauer spectra were obtained with a spectrometer described elsewhere (*7*). The radioactive source was ^{57}Co in a rhodium matrix.

Magnetization Measurements

Samples of Fe_2MoO_4 cooled to helium temperature in approximately zero field showed zero or very small magnetization, depending on their magnetic history. What magnetization they had ($<0.02\mu_B$) was thermally reversible, with an inversion point ~160°K [see Fig. 1]. Progressive application of a magnetic flux density up to 1 tesla (10 kG) at liquid helium temperature gave a nonlinear increase in magnetization, and there was a further increase on warming to ~50°K with the field (1 tesla) still on. Above this temperature the magnetization decreased, reaching a minimum at the inversion point [see Fig. 2]. On recooling the sample, the curve retraced its path as far as the maximum at 50°K, but continued to increase below this, attaining a value corresponding to $\sim 0.2\mu_B$ per formula at helium temperature. Further heating and cooling cycles with the field either on or off gave perfectly reversible behavior. In other words, the samples could not be fully magnetized by a flux density of 1 tesla at low temperatures, but a moment of $0.2\mu_B$/formula could be "frozen in" by cooling from above 50°K in this field. This "thermoremanent" behavior has been found to occur in cases of contiguous ferromagnetic and antiferromagnetic zones, where the anistropy

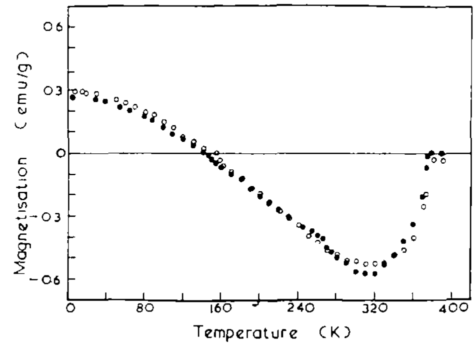

FIG. 1. Thermomagnetic curve of Fe_2MoO_4 in zero applied magnetic field. ○ = cooling; ● = warming.

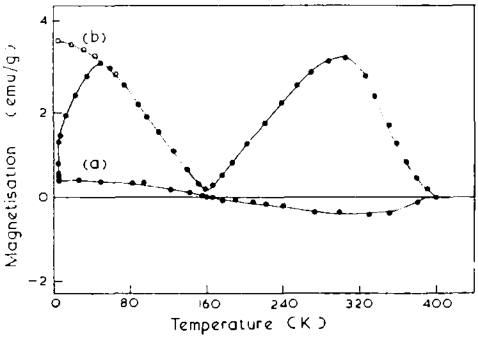

FIG. 2. Thermomagnetic curves of Fe_2MoO_4 in (a) zero field and (b) a field of flux density 1 tesla, showing thermoremanence below 50°K. ○ = cooling; ● = warming.

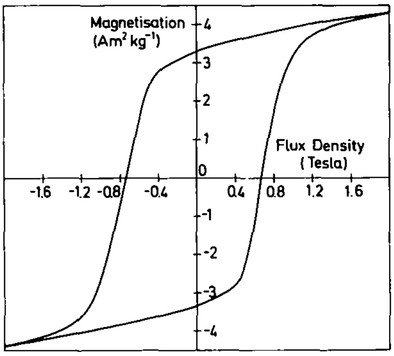

FIG. 3. Hysteresis loop of Fe_2MoO_4 at 5°K.

of the antiferromagnetic component tends to "lock in" the ferromagnetic moment (*8*, *9*).

The X-ray data give no indication of structural inhomogeneity or chemical impurity in these samples, so it is not suggested that there are distinct ferromagnetic and antiferromagnetic phases. Rather we think that the basic interactions in the ferrite phase are responsible for the behavior.

Thermoremanence due to an intrinsic mechanism has previously been reported in the inverse spinel Co_2VO_4 (*10*). The hysteresis loop for this compound shows a pronounced displacement along the magnetization axis, in contrast with the displacement along the field axis found for oxide-coated cobalt particles (*8*, *9*). We have therefore made hysteresis measurements on Fe_2MoO_4, after cooling to 5°K in a flux density of 2 tesla [see Fig. 3]. There is a slight shift along the field (flux density) axis, but certainly none along the magnetization axis. The coercivity, however, is abnormally large and the temperature variation of the coercivity was rather complex [see Fig. 4]. Apart from the expected singularity at the inversion point, the main feature is a sharp drop between 30 and 50°K to about one third of the low temperature value, suggesting the onset of a large exchange anisotropy below 50°K.

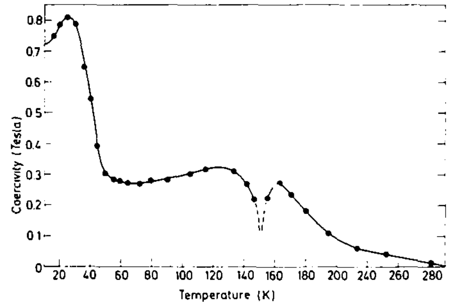

FIG. 4. Thermal variation of the coercive force.

Neutron Diffraction

From the neutron diffraction measurements on Fe_2MoO_4, and in particular from the absence of additional or satellite peaks below the Néel point, Abe et al. (*2*) concluded that the magnetic structure is "approximately" of Néel type: $Fe^{2+}(4\mu_B\downarrow)[Fe^{2+}(4\mu_B\uparrow)Mo^{4+}(0\mu_B)]O_4$, where the two 4*d* electrons of Mo^{4+} are in a low-spin state, having no resultatnt spin moment. However, as they point out, they would not have been able to discern a small deviation from the collinear Néel type arrangement, such as a canted or helical structure. Although they have a slight suspicion about the collinearity of the spins, they did not discuss the possibility of a strong A–A or B–B interaction, comparable to the A–B interaction, which is generally the cause of a breakdown of the Néel model.

As the magnetization measurements at temperatures lower than those used by Abe et al. indicated some very interesting results, we considered that further detailed neutron diffraction work was desirable. In particular we were interested in the effects of the application of a magnetic field at temperatures between liquid helium (4.2°K) and liquid nitrogen (77°K). As it was clear from the magnetization measurements that once a sample has been subjected to a magnetic field its characteristics changed irreversibly, a fresh sample was used for the neutron diffraction measurements.

The intensities of (111), (220), (311), (222), (400), and (331) peaks were studied at 4.2°K in increasing fields up to a flux density of 1 tesla, applied along the scattering vector. The computed integrated intensities of the (311), (220), (222), and (331) peaks showed very little change up to ~0.7 tesla and then decreased on further increasing the flux density to 1 tesla [see Fig. 5]. It should be

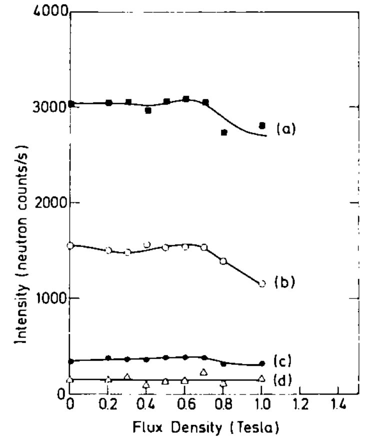

FIG. 5. Field dependence of diffracted thermal neutron beam at 4.2°K of (a) (311), (b) (220), (c) (222), and (d) (331) reflections.

mentioned however, that the gaussian fits to the (220) and (311) were not very good and we suspect the presence of satellite peaks which could not be successfully resolved.

The behavior of the (111) peak intensity was very interesting [see Fig. 6(b)]; the intensity increased with field up to 0.5 tesla, after which it behaved like the other peaks. This unusual behavior led us to study the intensity of the (111) peak at liquid nitrogen temperature in a applied field. After an initial drop the intensity changed very little at this temperature [see Fig. 6(c)].

The initial increase of the (111) peak intensity at 4.2°K with increasing magnetic field is consistent with a noncollinear spin arrangement (*11*), which probably changes to a collinear arrangement at 77°K.

The variation of the (400) peak intensity was also unusual [see Fig. 6(a)]: it did not change until 0.7 tesla after which it increased rapidly to a very high value.

According to Wilkinson et al. (*12*) the reflections which show the largest decrease in intensity indicate that the easy axis of magnetization is parallel to the scattering vector of those crystal planes. From our results it appears that (111) is probably the easy direction of spin in Fe_2MoO_4.

Mössbauer Spectroscopy

The Mössbauer spectrum of Fe_2MoO_4 was recorded at various temperatures between 4.2 and 295°K. The spectra were rather complex but the centroid (average chemical isomer shift) at room temperature relative to iron foil at room temperature was ~0.55 mm sec^{-1}; this is above the values normally encountered for high-spin Fe^{3+} in oxide

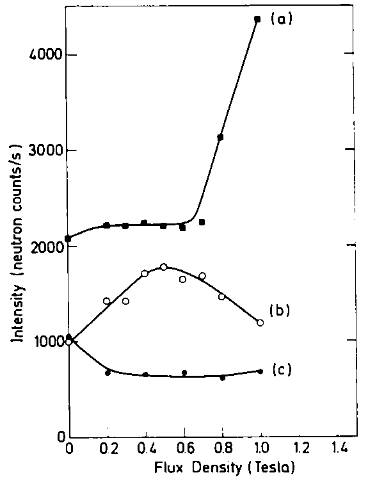

FIG. 6. Field dependence of diffracted thermal neutron beam at 4.2°K of (a) (400), and (b) (111) reflections and at 77°K of (c) (111) reflection.

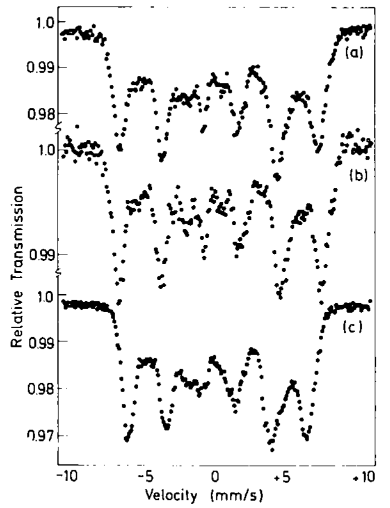

FIG. 7. Mössbauer spectra of Fe_2MoO_4 at (a) 80°K, (b) 50°K, and (c) 4.2°K.

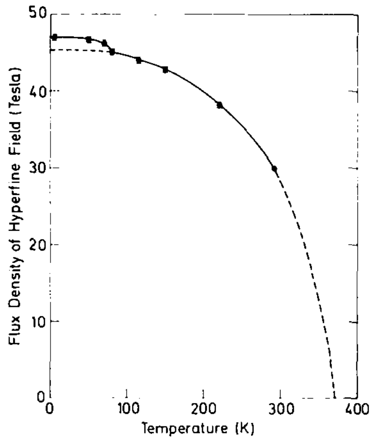

FIG. 8. Temperature dependence of the average hyperfine flux density at irion sites in Fe_2MoO_4.

phases and is consistent with the presence of high-spin Fe^{2+} (*13*). Likewise the magnitude of the hyperfine magnetic flux densities was typical of Fe^{2+} rather than Fe^{3+}, being about 44 tesla at room temperature. The spectra above liquid nitrogen temperature are similar to those recently published (*14*). It was not possible to resolve these complex spectra but at temperatures below 70°K, two small additional peaks appeared at the centre. In addition some of the main peaks broadened below 70°K [see Fig. 7]. The thermal variation of the flux density of the hyperfine field is shown in Fig. 8; there appears to be a sudden increase below 70°K.

Discussion

The neutron diffraction results show distinct evidence of a transition from canted to collinear spin arrangement between 4.2 and 77°K, and it seems natural to associate the sharp coercivity drop at around 40°K with this transition. In addition the change in the thermal behavior of the hyperfine field below 70°K in the Mössbauer results indicates a change in magnetic structure as was observed in case of $FeCr_2O_4$ (*15*). The presence of the two small peaks in this low temperature region may also be due to this effect. From molecular field calculations Lotgering (*16*) predicted that spinels in which the B–B interaction is slightly smaller than the A–B interaction, there is a transition from a noncollinear spin arrangement to a collinear arrangement followed by a compensation point at a higher temperature; but so far as we are aware no previous example of this class of ferrimagnetism has been reported.

Lotgering proceeds by subdividing the A sublattice into two parts, and the B sublattice into four. Such a subdivision would seem appropriate when there are two types of magnetic ion on the B sublattice, and the internal ordering of each type can conceivably be either ferromagnetic or antiferromagnetic, as is the case with Fe_2MoO_4. In addition to the classes predicted by Néel and Yafet and Kittel several new types of ferrimagnetic order are anticipated, involving transitions from canted to collinear spin arrangements. An important corollary of Lotgering's theory is that canted spin arrangements always give rise to 'normal' magnetization curves, so that spin arrangements must be collinear in the vicinity of an inversion point. According to this model, the transition to noncollinearity below an inversion point involves canting on the B sublattice only, the spins on the A sublattice remaining aligned. The magnetization in the noncollinear state is then given by

$$\sigma_M = |M_A(T)\ \{(1/\beta) - 1\}|$$

where $M_A(T)$ is the magnetization of the A-sublattice, and β is the molecular field parameter representing the ratio of the BB and AB interactions. For Fe_2MoO_4, $M_A = 4\mu_B$ per formula, while $\sigma_M \simeq 0.2\mu_B$/formula, giving $\beta = 0.95$. If the Mo^{4+} ion is assumed to have a spin of $2\mu_B$, Lotgering's analysis predicts the transition from noncollinear to inversion behavior only if $0.67 < \beta < 1$, which is entirely consistent with the above value. In addition, for a β-value of 0.95, the molecular field parameter α for the A sublattice can take any value less than 1. If the value assumed for the Mo^{4+} spin is reduced below $2\mu_B$, the range of α and β values for which this type of behavior occurs is increased. However, a minimum value for the molybdenum moment is implied by the condition that the vector sum of the B sublattice moments, in the noncollinear state, must exceed that of the collinear A sublattice moments by an amount equal to the observed magnetization at $T = 0^\circ$K. Hence, the molybdenum moment must be greater than $0.2\mu_B$.

The amount of information obtainable from magnetic measurements is limited by the impossibility of measuring the paramagnetic Curie point and Curie constant, because of the dissociation of the compound. Nevertheless, interpreted on the basis of Lotgering's model, the magnetic data for Fe_2MoO_4 are entirely consistent with a high-spin Mo^{4+} with a moment of $2\mu_B$.

Finally we would like to add that Fe_2MoO_4 differs from Fe_2TiO_4 in which Ti^{4+} ($3d^0$) has zero spin and the magnetic interactions are entirely due to Fe^{2+} in the octahedral and tetrahedral sites, respectively; this is indicated by a much higher Néel temperature of the former, i.e., 370°K compared to 150°K. Also, the coercivity curve for Fe_2MoO_4 [Fig. 4] is not normal, as is the case for Fe_2TiO_4 (*17*). If Mo^{4+} ($4d^2$) was not contributing towards the magnetic interactions of this compound a Néel temperature comparable to 150°K would have been expected. In our view this again indicates that the Mo^{4+} is in an $S = 1$ rather than an $S = 0$ state in Fe_2MoO_4. Further experimental and theoretical work on the neutron diffraction intensities of Fe_2MoO_4 is being undertaken.

Acknowledgments

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