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The Magnetic Structure of MnCr₂O₄*

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Neutron diffraction patterns were obtained from $MnCr_2O_4$ at 300°K, 77°K, 20°K and 4.2°K. $MnCr_2O_4$ is a regular spinel with an oxygen parameter equal to 0.389. The Néel temperature was found to be 43°K in good agreement with magnetic measurements. At 18°K a further ordering sets in which results in a large number of superlattice lines which cannot be indexed on the basis of the spinel unit cell. The model of Kaplan *et al.* which postulates a ferrimagnetic spiral is shown to be in semi-quantitative agreement with the observed low temperature pattern.

Introduction

The chromites form an interesting class of magnetic materials which crystallize with the spinel structure. They generally have the so-called "regular" structure and are characterized by magnetic transition temperatures which are much lower than the corresponding ferrites. The Néel theory, which has been so successful in quantitatively explaining the magnetic properties of the ferrites, does not appear to be adequate for the chromites. The theory of Yafet and Kittel (Y-K) has therefore been used to account for the magnetic behavior of some chromites. In 1954 we reported some neutron diffraction experiments on MnCr₂O₄ which showed some features which could not be explained by the Y-K theory. Recently Kaplan, Dwight, Lyons and Menyuk have treated the problem of the ground spin-state in spinels. They have shown that over a range of the ratio, J_{A-B}/J_{B-B} , the rigorous solution to this problem, assuming a classical Heisenberg exchange interaction, consists of spirals. We have attempted to fit their model to our neutron diffraction data and have achieved a limited amount of success indicative of the general overall validity of the model.

Preparation and experimental data

The MnCr₂O₄ was prepared by Dr. Aaron Wold of the Lincoln laboratory using a "precursor" method, i.e. $MnCr_2O_7 \cdot 4C_3H_5N$ was crystallized, ignited and fired at 1100°C in air and quenched from 800°C. The preparation was then refired at 1100°C in an atmos-

phere of hydrogen diluted with nitrogen (1: 3) to reduce all the manganese to the divalent state. The measured ratio of Cr/Mn was $2.015\pm.002$ and the measured saturation magnetization at 4.2° K was $1.20 \ \mu_{B}$ per molecule.

Powder neutron diffraction diagrams were obtained at room temperature, liquid N₂, H₂ and He temperatures. The room temperature data gave excellent agreement with a regular spinel model having an oxygen parameter of 0.3892±.0003. In the liquid nitrogen pattern there is some evidence of short range ordering in the neighborhood of the forbidden (200) reflection. The Néel temperature as determined by the magnetic scattering in the (111) reflection was 46°K. The liquid H₂ pattern shows complete magnetic saturation in the fundamental reflections and a very marked short range ordering in the region around the (200) reflection. Just below this temperature (~20°K) a complex pattern of superlattice lines appears, which is not completely resolved. The fundamentals show no change at this transition. The pattern remains unchanged at 4.2°K. The most striking features of these superlattice reflections are the clustering of several into groups and the fact that they cannot be indexed until the unit cell is tripled in all dimensions. This cell $(3 \times$ 8.437 Å) is so large that the indexing is hardly significant.

Interpretation

Any analysis of the observed diffraction pattern at 4.2°K must account for both the magnetic scattering in the fundamentals as well as for the superlattice lines and be con-

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sistent with the observed microscopic moment. Assuming a Néel model, the magnetic scattering in the fundamentals can be used to determine the magnetic moments associated with the A (Mn^{+2}) and B (Cr^{+3}) sites. Such an analysis yields 3.56 μ_B and 1.50 μ_B respectively. Both are therefore much less than the corresponding spin-only values, and furthermore give a saturation magnetization of 0.56 $\mu_{\rm B}$ per molecule as compared with a measured value of $1.20 \mu_{\rm B}$. In addition there is no possible explanation of the superlattice reflections. The Néel model is therefore not applicable and one can also show, as seen by the following argument, that the Y-K model also fails. The moments associated with the A and B sites are both much smaller than the expected values and hence one would have to invoke angles on both sites which is not allowed by the Y-K model. Furthermore, even if one assumed angles on both sites these would presumably be ordered. One would naturally try to associate the observed superlattice lines with this ordering. However the superlattice structure first appears at a much lower temperature ($\sim 20^{\circ}$ K) than the magnetic transition. A careful comparison of the magnetic contribution to the fundamentals just above the superlattice ordering temperature with that at 4.2°K shows no change indicating that the reduction in the A and B site moments takes place without the formation of the Y-K substructures.

The model proposed by KDLM leads to a ferrimagnetic spiral structure. There are three sublattices, one containing the A sites and the other two the B sites which have

been divided as in the Verwey ordering of B sites in $Fe_{3}O_{4}$. On each of these sublattices the spins lie on cones with the axes arranged so that the A site cones are antiparallel to both sets of B site cones. The axial components give rise to the magnetization while the components perpendicular to the axes rotate with a common propagation vector, but with differences in phase. These rotating components give rise to the superlattice reflections whereas the axial components contribute to the fundamental reflections. The theory yields the following parameters as a function of the ratio, J_{A-B}/J_{B-B} ; the cone angles, the relative phase angles of the rotating components and the wavelength of the propagation vector. The direction of the propagation vector is also fixed, but the direction of the cone axes is left undetermined. If one assumes a spin-only value for the moments, then there is a unique set of cone angles whose axial components are such that they add up to the observed saturation magnetization. This can be used to fix the ratio, J_{AB}/J_{BB} , and hence the other two parameters. Several different calculations have been performed and there is general semiquantitative agreement between the observed and calculated intensities of both the fundamental and superlattice reflections, as well as the positions of the superlattice reflections. It is thought that this model provides a good first order approximation to the structure and that further refinements in the theory as well as single crystal experimental data will result in rather minor modifications.

DISCUSSION

E. W. GORTER: 1) Could you tell us how far your experiments prove the Kaplan model, i.e. have you been able to exclude all simpler models?

2) Do the cone angles on A and B sites correspond to a combination of these angles for a certain value of BB/AB interaction ratio as given by Kaplan?

J. M. HASTINGS: In answer to the first part of your question, it is our conclusion that the experimental data represent an excellent check on the theory of Kaplan *et al.* in the following sense. The theory was able to index the pattern and account for the intensity in a semi-quantitative manner. This, I believe, indicates that we have a good first approximation to the structure. Further improvements in the theory, such as inclusion of second neighbor B-B interactions, and extension of the range to even smaller values of the ratio J_{A-B}/J_{B-B} will probably result in rather minor changes in the model.

As for the second part of your question, I would point out that the theory predicts

different cone angles for all three, (A, B₁, B₂), sublattices.

T. KAPLAN (Reply to E. W. GORTER): Dr. Hastings summarized the main points quite well. I might add that, although we have considered only nearest neighbor A-B and B-B interactions, there is reason to expect that other B-B interactions are important. This reason is the fact that $ZnCr_2O_4$ was found by Corliss and Hastings to show long range order, coupled with Anderson's result that nearest-neighbor interactions could not produce such order. The other possible source of error mentioned by Hastings, namely that we do not have the exact ground state, is much more difficult to evaluate.

R. NATHANS: Did you work in the impure $MnCr_2O_4$ give you any idea as to what these impurities do to the magnetic structure?

J. M. HASTINGS: The difference in the two samples may be characterized by saying that the old one appeared to have much broader super-lattice lines which reduced the resolution to the point where the interpretation of the data was an almost hopeless task. This broadening is probably due to a variation in the magnitude of the propagation vector.

W. P. Wolf: Since the exchange interaction is relatively small in these chromites would you not expect an appreciable influence on the canting arrangement from local crystalline field anisotropy?

T. KAPLAN: We expect the anisotropy forces to be much smaller than the dominant exchange forces. Maybe some of the small peaks and other details will be affected by anisotropy.

J. M. HASTINGS: I think that the appearance of short range order at room temperature, which is well above the transition temperature, is a more appropriate measure of the strength of the magnetic interaction. If this is correct, then one would conclude that crystal field effects would be a very small perturbation.

E. W. GORTER: This is one case in which the crystalline field does influence the spin structure. N. Sakamoto and Y. Yamaguchi describe the magnetic properties of Co [CoTi] O₄ in this conference (these Proceedings, Vol. I., p. 276). The saturation moment is smaller than should be expected from the difference in moments for $(Co)_A$ and $(Co)_B$. The explanation in this case (see discussion by J. Smit after the Sakamoto's paper) is probably that the moments in B sites are non-parallel because the spin orientation of $(Co)_B$ caused by the crystalline field can compete with the (weak) AB Co-Co interaction.