Structural and Magnetic Phase Transitions in $ZnCr_2O_4$

M. K. Crawford,[1] R. L. Harlow,[1] E. M. McCarron,[1] R. Flippen,[1] P. L. Lee,[2] Y. Zhang,[2]
J. Hormadaly,[3] B. Woodfield,[4] R. Stevens,[4] J. Boerio-Goates,[4] Q. Huang,[5] J.W. Lynn[5]
[1]DuPont Central Research and Development Department, Wilmington, DE, U.S.A.
[2]Advanced Photon Source, Argonne National Laboratory, Argonne, IL, U.S.A.
[3]Ben-Gurion University of the Negev, Beer-Sheva, Israel
[4]Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT, U.S.A.
[5]National Institute of Standards and Technology (NIST), Center for Neutron Research, Gaithersburg, MD, U.S.A

Introduction

There is a considerable amount of interest in the behavior of magnetic materials that are geometrically frustrated [1]. Geometric frustration occurs when magnetic ions are located on lattice sites that lie at the vertices of equilateral triangles and when the magnetic coupling/magnetic anisotropy is such that all three ions on a triangle can not simultaneously be in the minimum energy configuration with respect to their nearest neighbors.

Spinels, whose general chemical formula is AB_2O_4, exist for a large variety of A and B ions. The spinel B sublattice is geometrically frustrated since the B ions are located on the vertices of tetrahedra, fulfilling the triangular condition. $ZnCr_2O_4$ is perhaps the best-known example of a spinel that exhibits clear evidence of magnetic frustration [2]. Figure 1 shows a structural diagram of the spinel unit cell, and Fig. 2 shows two views of the spinel B sublattice.

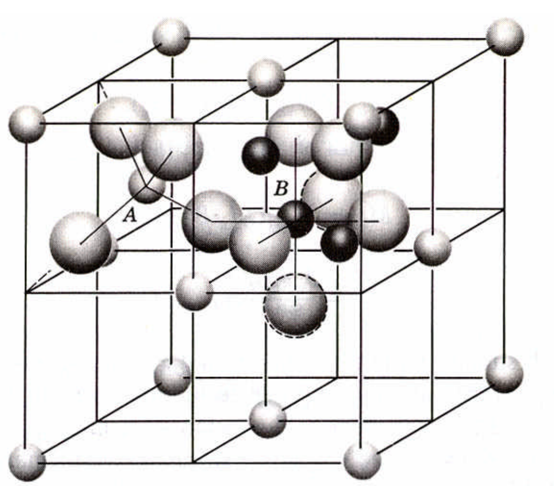

FIG. 1. Unit cell of $ZnCr_2O_4$ (A = Zn, B = Cr), an example of a normal spinel. The space group symmetry is Fd-3m at room temperature, with eight formula units per unit cell, and a = 8.3303 ±1 Å from neutron diffraction. (From Physical Principles of Magnetism, *by A. H. Morrish, Wiley, New York, NY, 1965, p. 502).*

Here we describe the results of high-resolution synchrotron powder x-ray diffraction measurements of $ZnCr_2O_4$, a compound known to undergo a subtle structural phase transition (SPT) at a temperature close to the temperature at which long-range antiferromagnetic order appears (T_N ~ 10 K).

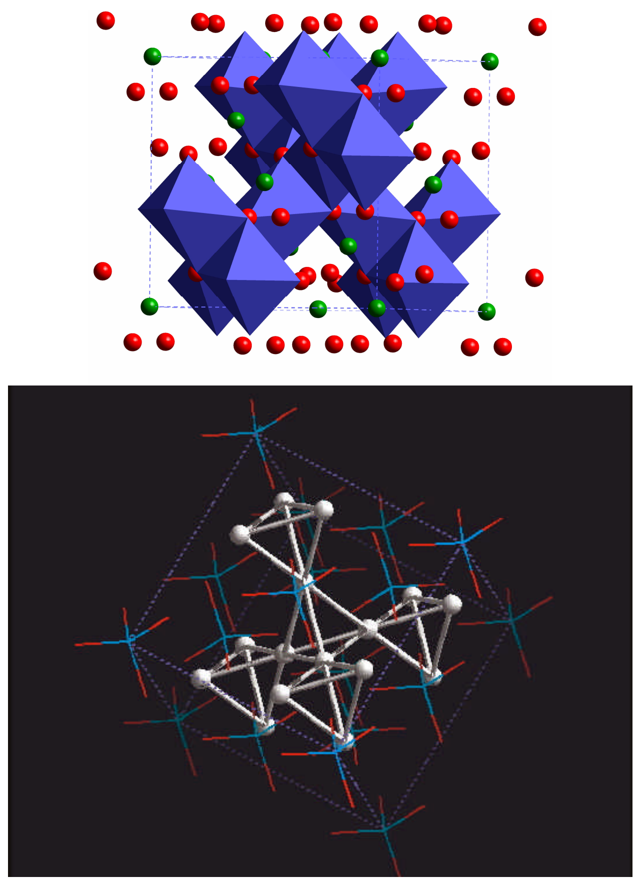

FIG. 2. Two views of the B sublattice of $ZnCr_2O_4$. Top shows the octahedral oxygen coordination of the Cr^{3+} ions. Oxygen octahedra are blue, Zn ions are green, and oxygen atoms coordinated to Zn are red. Bottom shows five magnetically frustrated tetrahedra (outlined in white). White spheres are the Cr^{3+} ions located at the vertices of the tetrahedra.

In this work, our objectives were to (1) precisely determine the SPT temperature for comparison with T_N, and (2) establish the order of the SPT. These issues are important since theories [3, 4] of magnetism in these materials invoke a new type of spin-lattice coupling, which leads to spin-Peierls order in 1-D materials but is not known in 3-D materials.

Results

Figure 3 shows the high-temperature inverse magnetic susceptibility and an expanded view of the low-temperature region of the magnetic susceptibility. From a Curie-Weiss fit to the high-temperature susceptibility, the Cr^{3+} magnetic moment $\mu = 3.89\ \mu_B$, which is nearly equal to the spin-only value of $3.87\ \mu_B$, indicating that the orbital magnetic moment is fully quenched. The Weiss constant $\theta_W = -384$K, suggesting that there is strong antiferromagnetic coupling among the Cr^{3+} ions. Nevertheless, the magnetic susceptibility data in Fig. 3 indicates a low value of $T_N = 10.7$K (midpoint of the transition). In fact, the ratio $f \equiv \theta_W/T_N$ has been identified as a measure of the degree of frustration [1]. Values of f in excess of 10 are interpreted as evidence for strong geometric frustration. The f value for $ZnCr_2O_4$ is 35.9, so this material is very strongly frustrated.

Figure 4 shows x-ray powder diffraction scans of the (800) Bragg reflection (indexed to the high-temperature cubic unit cell) at five temperatures going through T_N. The (800) reflection splits into (800, 080) and (008) reflections, with a two-phase coexistence region about 1.5K in width. These high-resolution data demonstrate

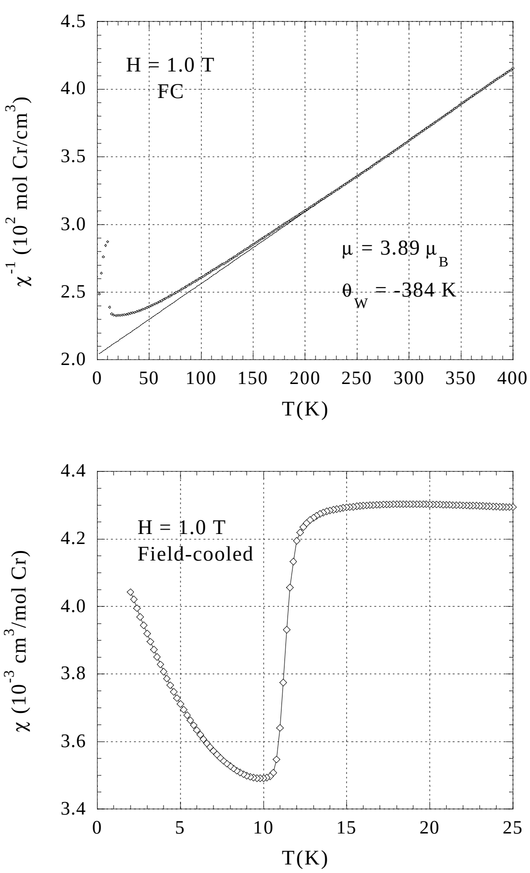

FIG. 3. Field-cooled inverse magnetic susceptibility and Curie-Weiss fit (top) and magnetic susceptibility (bottom) vs. temperature.

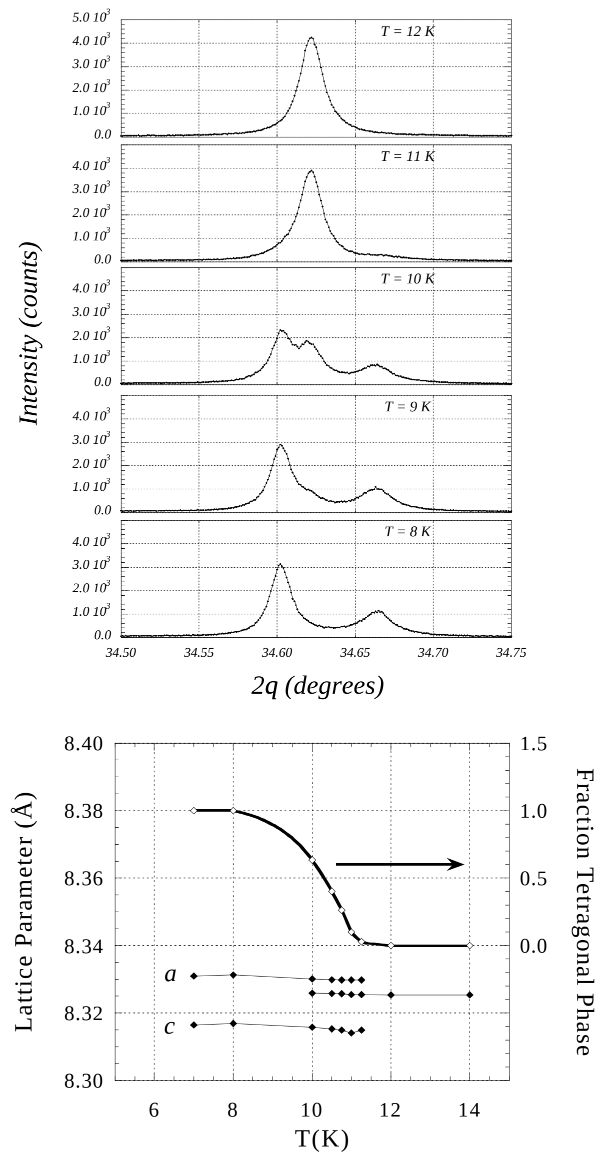

FIG. 4. (Top) The (800) Bragg reflection as a function of temperature for $ZnCr_2O_4$. (Bottom) Lattice parameters and fraction of sample converted to the low-temperature tetragonal phase vs. temperature for $ZnCr_2O_4$. The c/a ratio for the tetragonal phase is 0.9983 at T = 7K.

that the SPT is of first-order. Figure 4 also shows the cubic and tetragonal lattice parameters as functions of temperature, which clearly change discontinuously at the SPT, as expected for a first-order SPT. A similar result has been reported by using neutron diffraction [5], although observation of a two-phase region was not described there.

Discussion

Comparison of the synchrotron x-ray data and the magnetic susceptibility data show that the magnetic and structural phase transitions occur very near to each other in temperature. A precise comparison is somewhat difficult, since the first-order structural phase transition has a two-phase coexistence region with a width of about 1.5K, while the magnetic transition occurs over a temperature interval of 1.3K. Nevertheless, the magnetic transition is essentially complete at a temperature of 10.8K (at applied magnetic fields of 1.0T or 10 Oe, suggesting that the same would also be true in zero field), whereas the SPT is only 25% complete at that temperature. These data suggest that the magnetic transition occurs at a slightly higher temperature than the structural transition. On the other hand, predictions based on a Landau theoretical treatment of the coupled lattice-spin system suggest that a spin-Peierls state, which leads to the tetragonal lattice distortion, will either precede in temperature, or coincide with, the transition to Néel order [4]. Our data appear to be inconsistent with that prediction, whether the transition we observe in the magnetic susceptibility is a spin-Peierls transition or a Néel transition. In either case, one would expect the structural distortion to occur at the same temperature as the magnetic transition. However, before we can reach a firm conclusion it will be necessary to establish the absolute accuracies of the temperature sensors on the different cryostats to a level considerably better than 1K.

In conclusion, we have used the high resolution of synchrotron x-ray powder diffraction to study the subtle structural phase transition in the highly frustrated antiferromagnet $ZnCr_2O_4$. The data clearly show two-phase coexistence and a discontinuous change of lattice parameters, which establishes that the SPT is first-order. The data also suggest that the magnetic transition occurs at a slightly higher temperature than the SPT, but the absolute accuracies of the temperature measurements must be determined to verify this conclusion.

Acknowledgments

Use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. We also acknowledge the support of the Synchrontron Radiation Instrumentation Collaborative Access Team (SRI-CAT). The $ZnCr_2O_4$ sample was supplied by S. Ziemniak of Lockheed Martin Corporation, Schenectady, NY.

References

[1] A.P. Ramirez, in *Handbook of Magnetic Materials*, Vol. 13, edited by K. H. J. Buschow (Elsevier, New York, NY, 2001), pp. 423-520; also A. P. Ramirez, Ann. Rev. Mat. Sci. **24**, 453 (1994).

[2] H. Martinho, N. Moreno, J. A. Sanjurjo, C. Rettori, A. J. Garcia-Adeva, D. L. Huber, S. B. Oseroff, W. Ratcliff II, S.-W. Cheong, P. G. Pagliuso, J. L. Sarrao, and G.B. Martins, J. Appl. Phys. **89**, 7050 (2001).

[3] Y. Yamashita and K. Ueda, Phys. Rev. Lett. **85**, 4960 (2000).

[4] O. Tchernyshyov, R. Moessner, and S. L. Sondhi, Phys. Rev. Lett. **88**, 067203-1 (2002).

[5] S.-H. Lee, C. Broholm, T. H. Kim, W. Ratcliff II, and S.-W. Cheong, Phys. Rev. Lett. **84**, 3718 (2000).