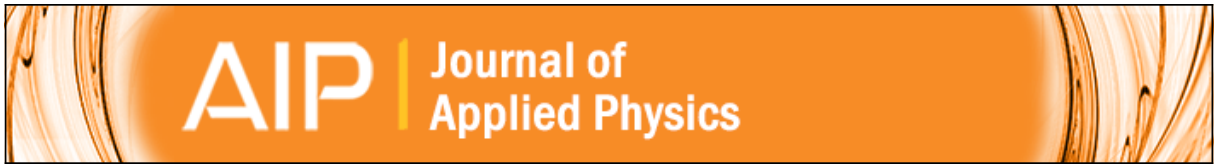

Studies of the three-dimensional frustrated antiferromagnetic ZnCr 2 O 4

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Studies of the three-dimensional frustrated antiferromagnetic $ZnCr_2O_4$

H. Martinho, N. O. Moreno, J. A. Sanjurjo, and C. Rettori
Instituto de Física ''Gleb Wataghin,'' UNICAMP, 13083-970 Campinas-SP, Brazil

A. J. García-Adeva and D. L. Huber[a)]
Physics Department, University of Wisconsin-Madison, 1150 University Ave., Madison, Wisconsin 53706

S. B. Oseroff
San Diego State University, San Diego, California 92182

W. Ratcliff II and S.-W. Cheong
Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854

P. G. Pagliuso and J. L. Sarrao
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

G. B. Martins
National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32306

Results of studies of the susceptibility, magnetic specific heat, and electron paramagnetic resonance spectrum of the geometrically frustrated antiferromagnetic $ZnCr_2O_4$ are presented. The temperature dependence of the susceptibility and the specific heat are in good agreement with the predictions of the quantum tetrahedral mean field model for exchange-coupled spin-3/2 ions on a pyrochlore lattice. The origin of the anomalous behavior of the resonance intensity below 90 K is discussed. [DOI: 10.1063/1.1358340]

I. INTRODUCTION

In recent years, the investigation of geometrically frustrated magnets has been recognized as an important and exciting area of research.[1,2] Among the systems studied, the pyrochlore antiferromagnets have received special attention. In the pyrochlore systems, the magnetic ions occupy the vertices of a three-dimensional array of corner-sharing tetrahedra. Various theoretical studies have established that the pyrochlore array does not undergo a phase transition at finite temperature when there are only nearest-neighbor interactions.[2] Longer range interactions, coupling to the crystal lattice and the presence of impurities and defects can induce transitions to states with long range antiferromagnetic (AFM) or spin glass order.

In this article, we report the results of variety of studies of the spinel $ZnCr_2O_4$, in which the Cr ions occupy sites on a pyrochlore sublattice. Since the orbital state of the Cr^{3+} ion is a singlet, spin-orbit effects are small, and the magnetic system can be regarded, in a first approximation, as an array of spins ($s=3/2$) coupled by the Heisenberg exchange interaction, $J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j$. Previous studies[3–5] have established that $ZnCr_2O_4$ undergoes a first order spin-Peierls transition at 12 K where the onset of long range AFM order is accompanied by a lattice distortion. We have carried out a series of measurements of the susceptibility, specific heat, and the electron paramagnetic resonance (EPR) spectrum of $ZnCr_2O_4$. It should be noted that this work is part of a larger study of the magnetic properties of the Cd-doped system $Zn_{(1-x)}Cd_xCr_2O_4$, the results of which will be published elsewhere.[6]

The remainder of the article is organized as follows: the results of the susceptibility and specific heat measurements are given in Sec. II, where the data are analyzed using a recently developed quantum tetrahedral mean field theory.[7] The EPR data for the integrated intensity of the resonance and the linewidth are presented in Sec. III. Section IV is devoted to a discussion of the results.

II. SUSCEPTIBILITY AND SPECIFIC HEAT

Previous measurements of the susceptibility of $ZnCr_2O_4$[3,8] yielded different values of T_N, and the paramagnetic Curie temperature, Θ: $T_N=9.5$ K, $\Theta=-330$ K (Ref. 3) and $T_N=16$ K, $\Theta=-392$ K (Ref. 7). We have measured the susceptibility on the same samples that were used in our specific heat and EPR measurements and obtained the results $T_N=12$ K and $\Theta=-388$ K. We have also measured the field dependence of the magnetization ratio, M/H, for applied field H in the range $0.2\,\mathrm{T}\leqslant H\leqslant 5$ T. We found that the magnetization ratio is weakly field dependent in the paramagnetic phase; in the AFM phase, M/H is noticeably field-dependent.

In Ref. 4, specific heat data were reported for $ZnCr_2O_4$ in zero field over the range $5\,\mathrm{K}\leqslant T\leqslant 25$ K. We have extended these measurements to cover the range $2\,\mathrm{K}\leqslant T\leqslant 300$ K. Data were taken both in zero field and in an applied field of 6 T. We found that the specific heat is only weakly field dependent, except in the vicinity of the phase transition, and that the onset of the phase transition is at approximately 12 K.

As noted in Sec. I, we have compared the zero-field susceptibility and magnetic specific heat in the paramagnetic phase with the predictions of the quantum tetrahedral mean

a)Electronic mail: huber@src.wisc.edu

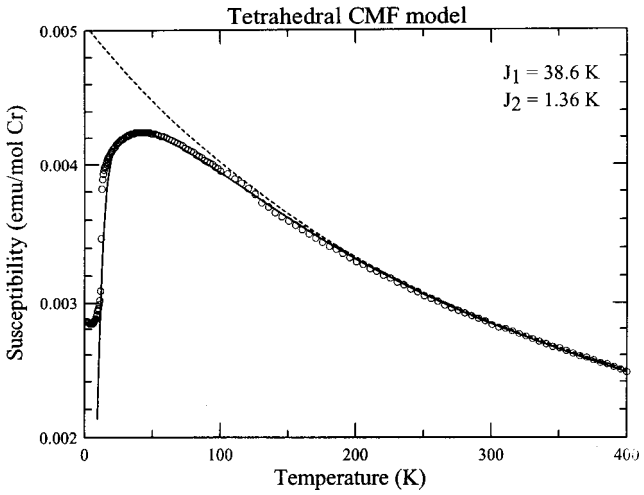

FIG. 1. Susceptibility of $ZnCr_2O_4$ in the paramagnetic phase. The data are shown as open circles. The solid line is the fit obtained using the quantum tetrahedral mean field approximation with $J_1=38.6$ K and $J_2=1.36$ K. The dashed line shows the Curie–Weiss approximation with $\Theta=-388$ K.

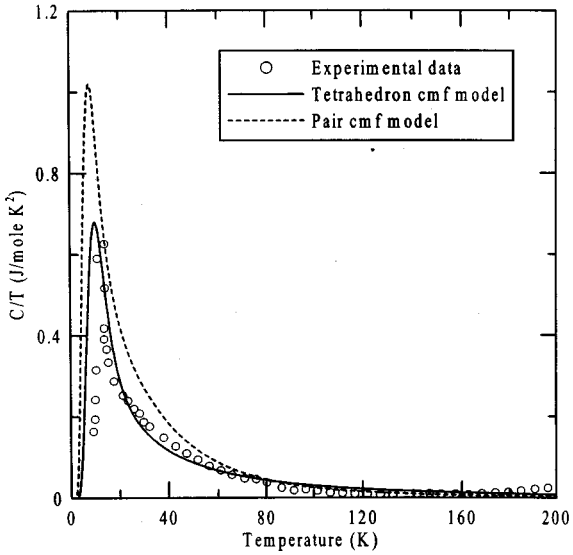

FIG. 2. Magnetic specific heat of $ZnCr_2O_4$ (obtained by subtracting the specific heat of $ZnGa_2O_4$ from the measured specific heat of $ZnCr_2O_4$). The data are shown as open circles. The solid line is the fit obtained using the quantum tetrahedral mean field approximation (tetrahedron cmf) with the nearest-neighbor exchange integral obtained from the fit to the susceptibility. The dashed line is the result obtained from a pair cluster mean field approximation (pair cmf) using the value $J_1=27$ K that was obtained by fitting the susceptibility (see Ref. 9).

field theory.[7] In the quantum tetrahedral mean field theory, the susceptibility per spin of the pyrochlore lattice (in units of $4\mu_B^2$) is expressed as

$$\chi^{\mathrm{tmf}}=\frac{\hat{\chi}^{\mathrm{tet}}(J_1,T)}{1+3(J_1+6J_2)\hat{\chi}^{\mathrm{tet}}(J_1,T)}, \tag{1}$$

where J_1 and J_2 are the nearest and next-nearest neighbor exchange integrals. The symbol $\hat{\chi}^{\mathrm{tet}}(J_1,T)$ denotes the susceptibility per spin of an isolated tetrahedron of spins and is written as

$$\hat{\chi}^{\mathrm{tet}}=\frac{\Sigma_S g(S)S(S+1)(2S+1)\exp[-J_1S(S+1)/2T]}{12T\Sigma_S g(S)(2S+1)\exp[-J_1S(S+1)/2T]}, \tag{2}$$

where the sum over S ranges from 0 to 6 in integer steps. The symbol $g(S)$ denotes the degeneracy factor, taking on the values 4, 9, 11, 10, 6, 3, and 1 for $S=0$, 1, 2, 3, 4, 5, and 6, respectively. Note that the total number of levels, $\Sigma_S g(S)\times(2S+1)$ is equal to 256 $[(2\cdot 3/2+1)^4]$.

In Fig. 1, we show the data for the susceptibility in the paramagnetic phase together with the fits obtained using quantum tetrahedral mean field approximation and the Curie–Weiss approximation, where $\chi^{\mathrm{CW}}=C/(T-\Theta)$. In the case of the tetrahedral analysis, the fit was obtained with $J_1=38.6$ K and $J_2=1.36$ K whereas χ^{CW} was calculated with $\Theta=-388$ K. It is apparent that there is excellent agreement between the data and the tetrahedral mean field model, which reproduces the peak in the susceptibility. In contrast, the susceptibility calculated in the Curie–Weiss approximation shows no peak, increasing monotonically with decreasing temperature.

The magnetic specific heat can also be calculated with the quantum tetrahedral mean field model, provided the next-nearest neighbor interactions are small in comparison with the nearest-neighbor coupling, as is the case with $ZnCr_2O_4$. The specific heat is readily expressed in terms of the derivative of the internal energy with respect to temperature. The internal energy per spin is given by $U=3J_1\langle \mathbf{S}_i\cdot\mathbf{S}_j\rangle$ where i and j are nearest neighbors and J_1 is the nn exchange integral. In the quantum tetrahedral mean field model, $\langle \mathbf{S}_i\cdot\mathbf{S}_j\rangle$ is related to $\hat{\chi}^{\mathrm{tet}}(J_1,T)$ through the equation $\langle \mathbf{S}_i\cdot\mathbf{S}_j\rangle=T\hat{\chi}_{\mathrm{tet}}-s(s+1)/3$. In Fig. 2 we compare the measured values of the magnetic specific heat with the predictions of the quantum tetrahedral mean field theory using the value of J_1 inferred from the fit to the susceptibility. The agreement is seen to be very good. It is worth noting that the peak in the specific heat in the cluster model, a short-range order effect, occurs at 9.9 K, which is close to the critical temperature associated with the onset of long range order. Also shown in Fig. 2 are the results obtained from a pair cluster mean field model, with J_1 (27 K) inferred from fitting the susceptibility.[9] In this case, the agreement is only qualitative.

III. EPR

Recently, Ohta *et al.* reported high-field measurements of the EPR spectra of $ZnCr_{2x}Ga_{2-2x}O_4$ that had been carried out using a millimeter wave spectrometer.[10] We have undertaken a complementary study of $ZnCr_2O_4$ at *X*-band frequencies where we investigated the temperature dependence of the integrated intensity of the resonance and the linewidth. In ''conventional'' (i.e., unfrustrated) antiferromagnets, the integrated intensity of the EPR signal has a temperature dependence that is similar to that of the static susceptibility. While we find this is the case for $ZnCr_2O_4$ above approximately 100 K, below this temperature, there is a qualitative difference in the behavior of the two. As noted, the susceptibility has a maximum at $\approx$40 K. At T_N, it has fallen to about 65% of its peak value; in contrast, the integrated intensity reaches

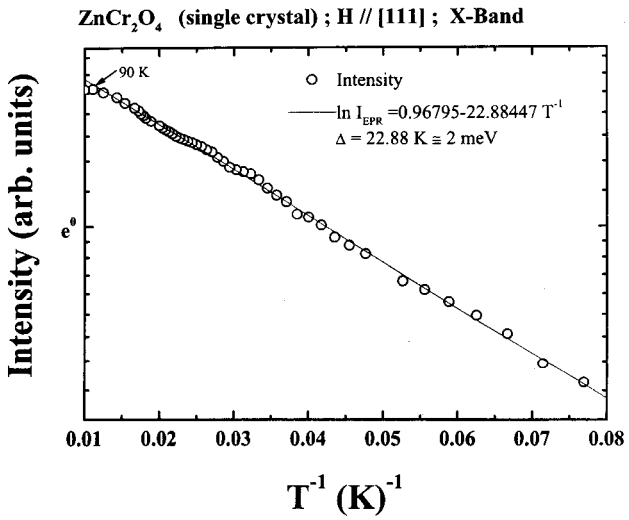

FIG. 3. Semilog plot of the integrated EPR intensity vs $1/T$ over the range $13\,\mathrm{K} \leqslant T \leqslant 100\,\mathrm{K}$. The temperature dependence corresponds to a gap ≈ 23 K.

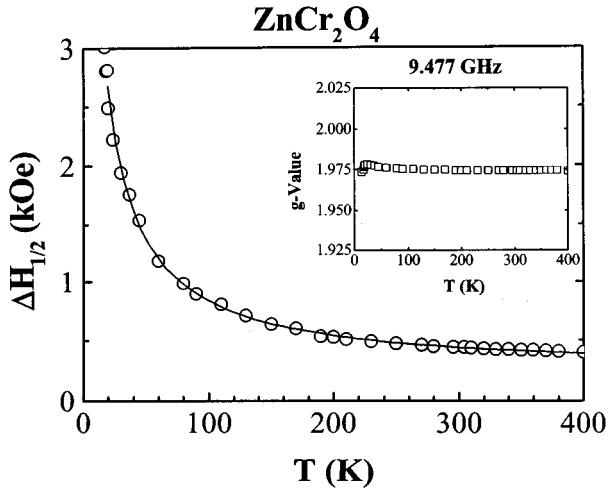

FIG. 4. EPR linewidth vs T. The solid line is the fit. The inset shows the behavior of the g factor.

a maximum at approximately 90 K. In the region $12\,\mathrm{K} < T < 90\,\mathrm{K}$, it decreases exponentially, as shown in Fig. 3, with a gap $\Delta \approx 23$ K (2 meV).

The integrated intensity of the EPR below 100 K is unusual in that its temperature dependence is qualititatively different from the temperature dependence of the susceptibility. To interpret this behavior, we make use of the Kramers–Kronig relation connecting the real and imaginary parts of the susceptibility. For our purposes, this relation can be expressed as

$$\chi(T) = 2\pi^{-1} \int_0^\infty d\omega \chi''(\omega, T) \omega^{-1}, \tag{3}$$

where $\chi''(\omega, T)$ denotes the imaginary part of the susceptibility and $\chi(T)$ is identified with the static limit of the real part of the susceptibility $\chi'(\omega, T)$. Since the absorbed power is proportional to $\int_{\omega_0 - \delta}^{\omega_0 + \delta} d\omega \omega \chi''$, where ω_0 is the resonance frequency and δ the linewidth, one would expect that the susceptibility and the integrated intensity would have a similar temperature dependence when the resonance is narrow, $\delta \ll \omega_0$, *provided* χ'' *has significant spectral weight only near* ω_0. Such would appear to be the case in $ZnCr_2O_4$ above 90 K. We interpret the behavior at lower temperatures as evidence for a growing contribution to the Kramers–Kronig integral for $\chi(T)$ coming from nonresonant modes. We conjecture that such modes, which are likely to be relaxational in nature, are characteristic of a frustrated paramagnetic at low temperatures.

In Fig. 4 we display the results obtained for the EPR linewidth and the g factor. The linewidth is approximately constant above 100 K. Below this temperature, the width increases, reaching a maximum at T_N. In contrast, the g factor is nearly temperature independent. In its temperature dependence, the EPR linewidth resembles the linewidth measured in unfrustrated antiferromagnets, where the width increases as $T \to T_N$ due to critical fluctuations.[11] To make this point more clear, we have fit the data to the standard expression $\Delta H_{1/2}(T) = \Delta H_{1/2}(\infty) + R/|T - T_N|^x$, and obtained the values $\Delta H_{1/2}(\infty) = 250(10)$ Oe, $R = 110(20)$ Oe K, $T_N = 12(1)$ K, and $x = 1.12(1)$.

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