Magnetic properties of the frustrated AFM spinel ZnCr$_2$O$_4$ and the spin-glass Zn$_{1-x}$Cd$_x$Cr$_2$O$_4$ ($x = 0.05, 0.10$)

H. Martinho, N.O. Moreno, J.A. Sanjurjo, and C. Rettori

*Instituto de Física "Gleb Wataghin", UNICAMP, 13083-970, Campinas-SP, Brazil.

A.J. Garcia-Adeva and D. L. Huber

*University of Wisconsin-Madison, Madison, WI, 53706, U.S.A.

S. B. Oseroff

*San Diego State University, San Diego, CA 92182, U.S.A.

W. Ratcliff II and S.-W Cheong

*Lucent Technology, Bell Laboratories, Murray Hill, N.J. 07974, U.S.A.

P.G. Pagliuso and J. L. Sarrao

*Los Alamos National Laboratory, Los Alamos, New Mexico 87545, U.S.A.

G. B. Martins

*National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32306, U.S.A.

Abstract

The $T$-dependence (2-400 K) of the electron paramagnetic resonance (EPR), magnetic susceptibility, $\chi(T)$, and specific heat, $C_v(T)$, of the normal antiferromagnetic (AFM) spinel ZnCr$_2$O$_4$ and the spin-glass (SG) Zn$_{1-x}$Cd$_x$Cr$_2$O$_4$ ($x = 0.05, 0.10$) is reported. These systems behave as a strongly frustrated AFM and SG with $T_N \approx T_G \approx 12$ K and $-400$ K $\gtrsim \Theta_{CW} \gtrsim -500$ K. At high-$T$ the EPR intensity follows the $\chi(T)$ and the $g$-value is $T$-independent. The linewidth broadens as the temperature is lowered, suggesting the existence of short range AFM correlations in the paramagnetic phase. For ZnCr$_2$O$_4$ the EPR intensity and $\chi(T)$ decreases below 90 K and 50 K, respectively. These results are discussed in terms of nearest-neighbor Cr$^{3+}$ ($S = 3/2$) spin-coupled pairs with an exchange coupling of $|J/k| \approx 50$ K. The appearance of small resonance modes for $T \lesssim 17$ K, the observation of a sharp drop in $\chi(T)$ and a strong peak in $C_v(T)$ at $T_N = 12$ K confirms, as previously reported, the
existence of long range AFM correlations in the low-$T$ phase. A comparison with recent neutron diffraction experiments that found a near dispersionless excitation at 4.5 meV for $T \lesssim T_N$ and a continuous gapless spectrum for $T \gtrsim T_N$, is also given.
Frustration in the antiferromagnetic (AFM) ordering of fcc and spinel lattices was recognized long ago by Anderson in his analysis of the highly degenerate magnetic ground state of these structures. This so-called geometrical frustration can prevent the system from undergoing spin-glass (SG) or AFM ordering down to temperatures much lower than the Curie-Weiss temperature, $T_G, T_N << |\Theta_{CW}|$. It has also been shown, theoretically and experimentally, that the ground state degeneracy can be removed by atomic disorder leading to a SG type of ordering. The AFM normal spinel ZnCr$_2$O$_4$ structure, in which the octahedral Cr sites form corner-sharing tetrahedra, as well as the pyrochlore and kagomé structures, are excellent systems to study the geometric frustration phenomenon. ZnCr$_2$O$_4$ has a very high Curie-Weiss temperature, $\Theta_{CW} \approx -400$ K, and a first order AFM transition at $T_N \approx 12$ K accompanied by a slight tetragonal crystal distortion ($\Delta a/a \approx 10^{-3}$). Besides, recent interesting low-$T$ neutron diffraction experiments showed, in the ordered phase ($T \lesssim T_N$), the existence of a near dispersionless excitation at 4.5 meV, and for $T \gtrsim T_N$, a continuous magnetic gapless density of states.

In this work we report on the $T$-dependence (2 - 400 K) of the electron paramagnetic resonance (EPR), magnetic susceptibility, $\chi(T)$, and specific heat, $C_v(T)$, in a single crystal of the normal spinel ZnCr$_2$O$_4$ of cubic structure ($Fd\bar{3}m$, O$_h^7$) and in the Cd doped polycrystalline Zn$_{1-x}$Cd$_x$Cr$_2$O$_4$ ($x = 0.05, 0.10$) compounds. A polycrystalline isomorphous compound of ZnGa$_2$O$_4$ was also used as a reference compound for the specific heat measurements.

II. EXPERIMENTAL DETAILS

Single crystals of ZnCr$_2$O$_4$ of typical size of $\sim 2\times2\times2$ mm$^3$ were obtained by the method of solid state reaction between stoichiometric amounts of Cr$_2$O$_3$ and ZnO in air. The crystals show natural growing (001), (111), and (011) faces that were checked by the usual Laue method. Polycrystalline Cd doped Zn$_{1-x}$Cd$_x$Cr$_2$O$_4$ ($x = 0.05, 0.10$) and ZnGa$_2$O$_4$ samples were prepared by the same method. The EPR experiments were carried out in a conventional ELEXSYS Bruker X-Band EPR spectrometers using a TE$_{102}$ room temperature cavity. The sample temperature was varied by a temperature controller using helium and nitrogen gas flux systems. This set up assures one that the spectrometer sensitivity remains about the same over a wide range of $T$. Magnetization measurements have been taken in a Quantum Design $dc$ SQUID MPMS-5T magnetometer. The specific heat was measured using the heat pulse method in a Quantum Design calorimeter using the QD-PPMS-9T measurement system.

III. EXPERIMENTAL RESULTS

For the ZnCr$_2$O$_4$ single crystal, as the temperature is lowered from room-$T$, the EPR line broadens and its intensity goes through a maximum at about 90 K with no measurable resonance shift. Figure 1 shows the $T$-evolution of the EPR spectra between 4 K and 45 K. For $T \lesssim 17$ K the resonance distorts and small resonances modes emerge at low-$T$. These
modes do not depend on whether the EPR spectra are taken under field cooling (FC) or zero field cooling (ZFC) conditions. But, they depend on the size and shape of the sample and show a slight orientation dependence (see inset). For $T \gtrsim 20$ K the EPR spectra show a single isotropic resonance. For the Cd doped samples the resonance also broadens, but the intensity increases down to $T \approx 12$ K (see below) where, again, the resonance distorts and small resonance modes are seen. These modes also show the same spectra under FC and ZFC conditions.

Figure 2 shows the $T$-dependence of the linewidth, $\Delta H_{1/2}$, and $g$-value between 18 K and 400 K for the crystal of Figure 1. The linewidth broadens at low-$T$, the $g$-value is $T$-independent and its value, $g = 1.978(5)$, corresponds to that of Cr$^{3+}$ ($3d^5$, $S = 3/2$) ions $g$-value in a cubic site. Both, the $g$-value and linewidth are isotropic for $T \gtrsim 20$ K. For the Cd doped samples similar resonance line broadening and $g$-values are obtained (not shown).

Figure 3 presents the $dc$ magnetic susceptibility, $\chi(T)$, corrected by the host diamagnetism in the range between 2 K and 400 K for the same crystal of Figure 1. FC and ZFC measurements at $H = 2$ kOe and 10 kOe gave no difference for the susceptibility data. At low field $\chi(T)$ shows the typical 3D AFM ordering with $\chi(T \rightarrow 0) \approx (2/3)\chi_{\text{max}}(T \approx 45$ K). The inset shows the sharp drop of the susceptibility at $T = 12(1)$ K. This temperature defines the Neél temperature, $T_N$, for the 3D long range AFM ordering in ZnCr$_2$O$_4$. The inset shows that, for $T \lesssim T_N$, the susceptibility is field dependent, $\chi(T, H)$. This has been attributed to domain wall movement in the AFM ordered state.

Figure 4 compares the magnetic susceptibility of the ZnCr$_2$O$_4$ single crystal of Figure 3 with those of the polycrystalline Zn$_{1-x}$Cd$_x$Cr$_2$O$_4$ ($x = 0.05, 0.10$) samples. For $T \gtrsim 100$ K the data for the three compounds can be fitted to the usual Curie-Weiss law. The linear fit yields to an effective number of Bohr magnetons $\mu_{\text{eff}} = 3.95(10) \mu_B$, as expected for Cr$^{3+}$ ($g = 1.978$, $S = 3/2$), and a Curie-Weiss temperature, $\Theta_{\text{CW}} = -390(20)$ K for ZnCr$_2$O$_4$. In a molecular field approximation $\Theta_{\text{CW}} = S(S+1) J_z/3k_B$. For $S = 3/2$, $z = 6$ (nearest-neighbors), and $\Theta_{\text{CW}} = -390$ K we obtain $J/k \approx -50$ K. The Curie-Weiss parameters for the Zn$_{1-x}$Cd$_x$Cr$_2$O$_4$ ($x = 0.05, 0.10$) samples are given in Table I. For $T \lesssim 100$ K Figure 4 shows, however, that there is a significant difference between the pure and Cd doped compounds. Low (high) field ZFC-FC measurements show, in the Cd doped samples, the typical SG irreversibility (reversibility) for $T \lesssim T_G \approx 12$ K (see inset of Figure 4). These results and the large values found for $|\Theta_{\text{CW}}|$ (see Table I), clearly indicate that the Cd doped samples develop a highly frustrated SG-type behavior with $T_G \approx 12$ K.

Figure 5 presents the $T$-dependence of the resonance intensity, $I(T)$, for the ZnCr$_2$O$_4$ single crystal and the polycrystalline Zn$_{1-x}$Cd$_x$Cr$_2$O$_4$ ($x = 0.05, 0.10$) samples. Using an EPR standard, we found that the intensity of the resonance at room-$T$, $I(300$ K), corresponds to the total amount of Cr$^{3+}$ ions present in the samples. Similar to the susceptibility data shown in Figure 4, here also we observe two $T$-regimes, above and below $T \approx 100$ K. For $T \lesssim 100$ K $I(T)$ shows significant difference between the pure and Cd doped compounds. For the Cd doped samples we found that $I(T)$ and $\chi(T)$ correlate well above $T_G \approx 12$ K (not shown); however, for the pure sample this correlation is only observed for $T \gtrsim 100$ K (see inset in Figure 5).

Figure 6 presents the $T$-dependence of the specific heat, $C_v(T)$, for the ZnCr$_2$O$_4$ single crystal, the polycrystalline Zn$_{1-x}$Cd$_x$Cr$_2$O$_4$ ($x = 0.05, 0.10$) samples, and the reference
compound ZnGa$_2$O$_4$. The inset shows the strong effect that the Cd impurities have on the AFM transition of the pure compound ZnCr$_2$O$_4$. The large reduction in the peak of the $C_T(T)$ confirms the assignment of SG character for the transition observed at $\approx 12$ K in the susceptibility data for the Cd doped samples. The transition temperatures, $T_G$ and $T_N$, are in fairly good agreement with those extracted from the susceptibility data (see inset in Figure 4). Fields up to 9 T, within the data resolution, did not affect $C_T(T)$ and the AFM and SG transitions temperatures.

IV. ANALYSIS AND DISCUSSION

The above EPR and magnetic susceptibility results show that the cubic normal spinel ZnCr$_2$O$_4$ and Zn$_{1-x}$Cd$_x$Cr$_2$O$_4$ ($x = 0.05, 0.10$) compounds present interesting magnetic behavior between 2 K and 400 K. A high-$T$ paramagnetic phase (HTPP), $T \gtrsim 100$ K for ZnCr$_2$O$_4$ and $T \gtrsim 12$ K for the Cd doped samples, and a low-$T$ order phase (LTOP), $T \lesssim 12$ K, AFM for the pure and SG for the doped compounds. For ZnCr$_2$O$_4$, a transition between these two regimes is observed in the interval between 12 K and 100 K. Our high-$T$ EPR results are in general agreement with those already reported for polycrystalline samples.$^{[4]}$ However, the low-$T$ EPR data for our ZnCr$_2$O$_4$ single crystal are quite different from those reported in Ref. 12. As the temperature decreases in the HTPP, the Cr$^{3+}$ magnetic moments experience short range AFM correlations. The evidence for it is that, for $T \gtrsim 2T_N$, the EPR resonance shows no $g$-shift and a $T$-dependence of the line broadening expected for a short range magnetic interaction in AFM materials above the Néel temperature $T_N$.\[[6]\]  

$$\Delta H_{1/2}(T) - \Delta H_{1/2}(\infty) = \frac{R}{|T - T_N|^x}$$  \hspace{1cm} (1)

The solid line in Fig. 2 shows the fitting of the data to Eq. 1. The fitting parameters are: $x = 1.12(1)$, $T_N = 12(1)$ K, $\Delta H_{1/2}(\infty) = 250(10)$ Oe, and $R = 110(20)$ Oe K$^x$. We should mention that, for $T \gtrsim T_N$, recent neutron diffraction measurements found a continuous gapless spectrum that was attributed to quantum critical fluctuations of small short range AFM correlated domains.$^{[4]}$ In the HTPP of ZnCr$_2$O$_4$, and for $T \gtrsim 100$ K, $\chi(T)$ and $I(T)$ follow the same $T$-dependence (see inset in Fig. 5), indicating that all the Cr$^{3+}$ ions that contribute to $\chi(T)$ also participate in $I(T)$. However, for $T \lesssim 100$ K, $\chi(T)$ deviates from $I(T)$, and they show maximums at $T \approx 40$ K and $T \approx 100$ K, respectively (see inset in Fig. 5). The maximum in $\chi(T)$ is caused by AFM correlations and indicates the onset of long range AFM ordering. Instead, the maximum in $I(T)$ can be interpreted as transitions within thermally populated exited states. The observation of EPR resonances in exited state levels of nearest-neighbor Cr$^{3+}$ spin-coupled pairs diluted in the spinel ZnGa$_2$O$_4$ has been reported by Henning et al.$^{[6]}$ These authors were able to determine, from the observed $I(T)$, the energy separation between the first exited triplet state ($S = 1$) and the ground singlet state ($S = 0$) to be $|J/k| \approx 32$ K. Also, from the optical spectra of the Cr$^{3+}$ spin-coupled pairs in ZnGa$_2$O$_4$ a value of $\approx 32$ K was measured for $|J/k|$.$^{[6]}$ Within the same scenario and taking into account the thermal population of all the exited states for the Cr$^{3+}$ spin-coupled pairs ($|S_1 + S_2| - |S_1 - S_2|; 3, 2, 1,$ and $0; S_1 = S_2 = 3/2$), the expected $T$-dependence of the
total EPR intensity, \( I(T) \), in the three exited states levels at energies \( J, 2J, \) and \( 6J \) above the singlet ground state is given by

\[
I(T) \sim \left[ A \exp(-J/kT) + B \exp(-3J/kT) + C \exp(-6J/kT) \right] / Z
\]  

(2)

where \( Z = 1+3\exp(-J/kT)+5\exp(-3J/kT)+7\exp(-6J/kT) \) is the partition function, the coefficients \( A, B, \) and \( C \) are adjustable parameters proportional to the transition probability within each excited multiplet. The solid line in the inset of the Figure 4 shows the \( T \)-dependence given by Eq. 2 for \( A = 10(2), B = 1(0.5), C = 4500(200) \) and \( J/k = -45(2) \) K. The value found for \( |J/k| \) is larger than the one (\( \approx 32 \) K) found for isolated \( \text{Cr}^{3+} \) spin-coupled pairs in \( \text{ZnGa}_2\text{O}_4 \). This difference is probably due to the different lattice parameters of \( \text{ZnCr}_2\text{O}_4 \) (\( a = 8.327 \) Å) in \( \text{ZnGa}_2\text{O}_4 \) (\( a = 8.37 \) Å). Nevertheless, the value is in good agreement with that extracted from the Curie-Weiss temperature, \( \Theta_{CW} \), (see above).

As we pointed out elsewhere, one can also attribute the difference between the temperature dependence of the susceptibility and the EPR intensity to the presence of non–resonant low frequency modes that contribute spectral weight to the Kramers–Kronig integral for the static susceptibility,

\[
\chi(T) = \frac{2}{\pi} \int_0^\infty d\omega \frac{\chi''(\omega)}{\omega},
\]

(3)

but do not participate in the EPR absorption. It is likely that such modes are seen in inelastic neutron scattering above \( T_N \). The fact that the susceptibility and the EPR intensity have a common temperature variation in the Cd–doped samples suggests that the non–resonant, low frequency modes, if present, are not making a significant contribution to the susceptibility integral.

Figure 7 shows the \( C_v/T \) plots obtained from the data of Figure 6 for each studied sample. The contribution from the magnetic component is obtained from the difference with the data for the non magnetic reference compound \( \text{ZnGa}_2\text{O}_4 \). The entropy, \( S \), is obtained integrating these differences and gives approximately the multiplicity of the involved levels, \( \approx 2^4 = 16 \). Within the same scenario of \( \text{Cr}^{3+} \) spin-coupled pairs, the Schottky anomaly for the spin-coupled pairs is given by:

\[
\frac{C_v}{T} = \frac{R}{T} \frac{\partial}{\partial T} \left[ T^2 \frac{\partial \ln Z}{\partial T} \right]
\]

(4)

Figure 8 shows the fitting of the data to Eq. 3. The obtained value for \( |J/k| = 35(2) \) K suggests the scheme of levels shown in Figure 8. The value found for \( |J/k| \) is consistent with those values obtained independently from the Curie-Weiss temperature, \( \Theta_{CW} \), and EPR intensity measurements in the HTPP (see above).

In the LTOP our EPR experiments show the appearance of small resonance modes (see Figure 1 for \( T \lesssim 17 \) K). We believe that their sample size and shape dependence and angular variation are, probably, more related to demagnetizing effects rather than to the tetragonal crystal distortion observed at \( T \approx 12 \) K. Besides, for \( T \lesssim T_N \) the magnetic susceptibility increases at higher fields (see inset of Figure 3) and also, a small increase is observed for \( T \lesssim 5 \) K (see Figure 3). These behaviors are similar to those observed in magnetization measurements of polycrystalline samples of \( \text{ZnCr}_2\text{O}_4 \) and they have been attributed to the
presence of AFM domains in the LTOP. Thus, we associate our resonance modes with AFM domains that might be present in these materials as a consequence of their highly frustrated 3D long range AFM magnetic structure.

V. CONCLUSIONS

In conclusion, our EPR and $\chi(T)$ results in the normal spinel ZnCr$_2$O$_4$ show, between 12 K and 100 K, a transition from a long to a short range regime of AFM correlations (LTOP-HTPP). From the $T$-dependence of the EPR intensity in the HTPP an exchange parameter of $J/k \approx -45$ K between the Cr$^{3+}$ ($S = 3/2$) spin-coupled pairs was extracted. This value is close to the one obtained independently from the Curie-Weiss temperature, $\Theta_{CW}$, and from the Schottky anomaly observed in the specific heat. Thus, the magnetic properties of these strongly frustrated systems in the HTPP can be described within a scenario involving just spin-coupling pairs of Cr$^{3+}$ ($S = 3/2$). The sharp drop in $\chi(T)$ at $T \approx 12$ K, the peak in $C_v(T)$ also at $T \approx 12$ K, and the ordering temperature extracted from the broadening of the EPR linewidth ($T_N \approx 12$ K) confirmed the AFM ordering at $T \approx 12$ K in ZnCr$_2$O$_4$. The resonance modes observed in the LTOP and the field dependent susceptibility, $\chi(T, H)$, indicates the presence of AFM domains in this material. Finally, we found that the disorder caused by the Cd impurities in ZnCr$_2$O$_4$ drives the system from an AFM to a SG type of highly frustrated magnetic ordering.

Although a model based on isolated pairs can account for many of the magnetic properties of ZnCr$_2$O$_4$, it does not include the interaction of the pairs with the surrounding ions. A widely used pair model that does include the effects of the interaction with neighboring spins is the constant coupling approximation. However, this model does not exploit the unique tetrahedral character of the Cr sublattice in ZnCr$_2$O$_4$. In particular, it predicts the same susceptibility for ZnCr$_2$O$_4$ as found in an unfrustrated simple cubic antiferromagnet, which has the same number of nearest neighbor interactions (6) and exhibits a conventional AFM transition. This contradiction has led two of us (AJGA and DLH) to develop a quantum tetrahedral mean field model. In this model, the energy levels of a four–spin tetrahedral cluster are calculated exactly and the interaction with the neighboring ions is treated in the mean field approximation. Good agreement with the susceptibility and the magnetic specific heat are obtained with nearest–neighbor interaction, $J_1 = 38.6$ K, and next–neighbor interaction, $J_2 = 1.4$ K.

VI. ACKNOWLEDGMENTS

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FIG. 1. $T$-evolution ($4 \, \text{K} \leq T \leq 45 \, \text{K}$) of the EPR spectra for a ZnCr$_2$O$_4$ single crystal. The inset shows the spectra at $T = 4 \, \text{K}$ for different field orientations in the (110) plane.
ZnCr$_2$O$_4$

$\Delta H_{1/2}$ (kOe) vs. $T$ (K)

$g$-Value

9.477 GHz

FIG. 2. $T$-dependence (18 K $\leq T \leq$ 400 K) of the EPR linewidth and $g$-value for the crystal of Fig. 1. The solid line shows the best fit of the linewidth to Eq. 1 (see text).
FIG. 3. \( T \)-dependence (2 K \( \leq T \leq 400 \) K) of the magnetic susceptibility, \( \chi(T) \), at \( H = 3 \) kOe (FC, ZFC). The inset shows the data for 2 K \( \leq T \leq 20 \) K and 0.2 T \( \leq H \leq 5 \) T.
FIG. 4. $T$-dependence ($2 \, \text{K} \leq T \leq 400 \, \text{K}$) of the FC magnetic susceptibility, $\chi(T)$, at 3 kOe for $\text{Zn}_{1-x}\text{Cd}_x\text{Cr}_2\text{O}_4$. The insets shows FC and ZFC data for $2 \, \text{K} \leq T \leq 50 \, \text{K}$ at $H = 100 \, \text{Oe}$ and 3 kOe.
FIG. 5. $T$-dependence ($15 \text{ K} \leq T \leq 400 \text{ K}$) of the EPR intensity, $I(T)$ for $\text{Zn}_{1-x}\text{Cd}_x\text{Cr}_2\text{O}_4$. The inset compares $I(T)$ and $\chi(T)$ for ZnCr$_2$O$_4$ and the solid line is the best fit of $I(T)$ to Eq. 2 (see text).
FIG. 6. $T$-dependence ($2 \text{ K} \leq T \leq 300 \text{ K}$) of the ZF specific heat, $C_v(T)$, for $\text{Zn}_{1-x}\text{Cd}_x\text{Cr}_2\text{O}_4$ and $\text{ZnGa}_2\text{O}_4$. The inset shows $C_v(T)$ for $2 \text{ K} \leq T \leq 300 \text{ K}$.
FIG. 7. $T$-dependence (2 K $\leq T \leq 300$ K) of the ZF $C_v/T$ for Zn$_{1-x}$Cd$_x$Cr$_2$O$_4$ and ZnGa$_2$O$_4$. The difference with the reference compound is also shown. The solid line gives the entropy, $S$, associated to the system’s level multiplicity.
$\text{Zn}_{1-x}\text{Cd}_x\text{Cr}_2\text{O}_4$

![Graph showing the magnetic contribution to $C_v/T$](image)

**FIG. 8.** $T$-dependence ($2 \text{ K} \leq T \leq 300 \text{ K}$) of the magnetic contribution to $C_v/T$. The dashed line is the Schottky anomaly calculated using Eq. 4 for a pair model of coupled $\text{Cr}^{3+}$ spins (see text).
### TABLE I. Curie-Weiss parameters for Zn$_{1-x}$Cd$_x$Cr$_2$O$_4$

| $x$ | $C$ (emu/mole Cr K) | $\theta_{CW}$ (K) | $\mu_{eff}$ ($\mu_B$) |
|-----|---------------------|-------------------|---------------------|
| 0.0 | 1.95(2)             | -390(20)          | 3.95(10)            |
| 0.05| 2.94(5)             | -500(20)          | 4.85(20)            |
| 0.10| 2.57(5)             | -483(20)          | 4.53(20)            |