Pressure-dependent magnetic properties of geometrically frustrated $ZnCr_2O_4$

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$ZnCr_2O_4$ is a *geometrically frustrated* antiferromagnet with a first-order transition at $T_N=12.5$ K, where it also undergoes a structural transition from cubic to tetragonal structures. Our pressure- and field-dependent magnetization measurements and our subsequent analysis using a quantum tetrahedral mean field theory are found to be consistent with theories based on spin-lattice coupling. We also found that there is a weak, but unquestionable, field-induced transition around 2.5 T, at which our magnetization shows a subtle anomaly and, at the same time, both the Néel point and the estimated gap energy exhibit a sharp increase. Another finding is that our high pressure data imply that there may well be a pressure-induced splitting in the ordering temperatures of the bond and spin order parameters.

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I. INTRODUCTION

In nature, there are various systems with a multitude of ground states. A prime example is spin glass,[1] which shows magnetic properties vastly different from those of well-ordered magnetic systems. To understand the nature of the ground state properties and the dynamics of such systems has far reaching implications on other seemingly unrelated problems such as protein folding.[2]

Unlike spin glass that has frustration in magnetic interaction due to disorder, there is a class of materials that have similar magnetic frustration although it has no disorder at all.[3] The frustration in these materials arises unexpectedly from purely geometrical coordinations of magnetic ions, so named as geometrically frustrated spin systems (GFSS). Compared with the well-studied spin glass systems, these GFSS have a chief obvious advantage. It is chemically pure, so can be more easily modeled and theoretically thoroughly studied than the spin glass.

In an ideal example of geometrically frustrated spin systems, the ground state ought to have no long-range order and instead forms a so-called spin liquid phase.[4] However, that it has no long-range order with a multitude of ground states seems to invite numerous possibilities of transforming itself into other types of the ground states with a long-range order when subject to otherwise harmless small perturbations. This phenomenon of order-by-disorder has since been observed in a few examples.[5] Similarly, these GFSS are sensitive to interactions of small magnitude that are bound to be present in a system even without doping. One such example is the spin-lattice interaction in $ZnCr_2O_4$.

$ZnCr_2O_4$ has Cr^{3+} at the B site of the spinel structure with $S=\frac{3}{2}$ spins on a lattice of corner-sharing tetrahedra: three $3d$ electrons occupy the low-lying t_{2g} triplet. Although Cr moments are fully frustrated because of the corner-sharing tetrahedra structure with strong antiferromagnetic interaction of $\Theta_{CW}\approx -390$ K and so expected to have no magnetic ordering at all, however, it undergoes a first order transition at 12.5 K from a paramagnetic phase with a cubic structure to an antiferromagnetic phase with a tetragonal structure. Upon cooling, the magnetization decreases before the actual antiferromagnetic transition at 12.5 K. One of the interesting features of $ZnCr_2O_4$ is that when it undergoes the first-order transition it develops a gaplike feature in the dynamical susceptibility measured by inelastic neutron scattering.[6] We note that this nondispersive mode is a characteristic feature of $ZnCr_2O_4$ as demonstrated by a subsequent theoretical work.[7] Therefore, it will be very useful to a further understanding of the gap feature if one can investigate it under external variations such as field and pressure.

The nature of the phase transition at 12.5 K has been theoretically studied by several groups.[7,8] According to these theories, the 12.5 K transition occurs through some kind of spin Jahn–Teller mechanism that distorts the structure to relieve the frustration, which then subsequently favors a Néel state. Interestingly enough, the two transitions, one a so-called bond order and the other the Néel order, occur at the same temperature. However, we should note that according to the theory it is also possible that the bond order precedes the Néel order depending on the details of interactions. This particular observation stresses the importance of the spin-lattice coupling in $ZnCr_2O_4$. Although external pressure is the best way of varying such spin-lattice coupling strength, to our knowledge there has been no report of pressure-dependent studies for $ZnCr_2O_4$.

In this work, we have measured the magnetization by varying magnetic field and pressure that should, *a priori*, be separately coupled to spin and lattice degrees of freedom. We will discuss our experimental findings in terms of a theoret-

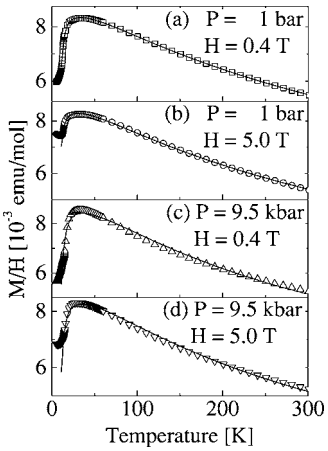

FIG. 1. Magnetic susceptibility taken at ambient pressure and 9.5 kbar. Solid lines are for the fitting results using the QTMFT model (see the text).

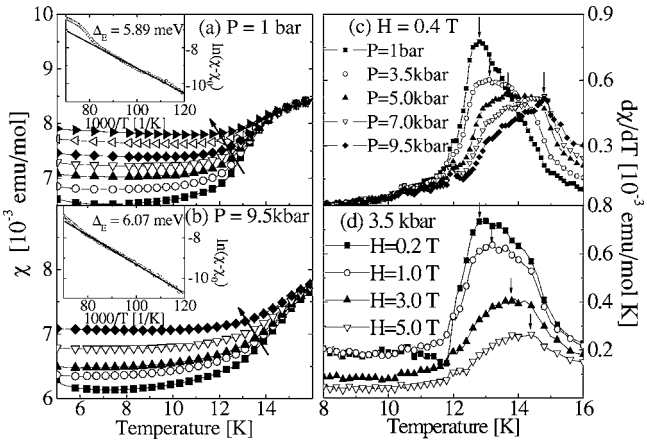

FIG. 2. An enlarged picture of the magnetic susceptibility taken at (a) ambient pressure and (b) 9.5 kbar near the transition temperature. The arrows in (a) and (b) indicate the direction of increasing fields from 0.2 to 5 T. The two insets show how we estimated the gap energy Δ_E, using a plot of $\ln[\chi(T)-\chi_0]$ vs $1/T$, where $\chi(T)$ is the susceptibility measured at T and χ_0 the magnetic susceptibility estimated at $T=0$ K. The lines in the insets represent the fitting results with the gap value shown in the figures (see the text). Temperature derivatives of the susceptibility, $d\chi/d$T, for the data taken at (c) five pressures with $H=0.4$ T and (d) four representative fields with 3.5 kbar. The arrows in (c) and (d) indicate the determined transition temperatures.

ical model and unravel another aspect of the spin-lattice coupling. From this study, we have also found a possibly field-induced metamagnetic transition.

II. EXPERIMENTAL DETAILS

Our polycrystalline sample was prepared in the same way as described elsewhere.[6] We cut the sample in a cylindrical shape with the dimensions of less than $2\phi \times 2$ mm.[2] dc magnetization measurements were performed using a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS5) with fields up to 5 T. Hydrostatic pressure was generated up to 9.5 kbar by using a homemade Cu-Be cylinder cell,[9] in which a 1:1 mixture of Fluorinert FC70 and FC77 was used as a pressure transmitting medium. Our pressure values were calibrated against the pressure dependence of the superconducting transition point of Sn. For each pressure and field configuration, we measured the empty cell, and subtracted off the background signals from the actual data taken with the sample put inside the cell in order to reduce any undesirable effects due to signals from the pressure cell. Although the background signals are small compared with the sample signals, nevertheless they can influence our estimate of the J_1 and J_2 values in our analysis. Thus all our data presented below are given after the careful background subtraction process.

Although there is usually a pressure drop of less than 3 kbar for a self-clamping pressure cell with cooling from room temperature to low temperature,[10] we think that most of our discussions would not change by such a pressure drop as we concentrate mostly on the low temperature properties in this work, except for when we analyze the temperature dependence of the magnetization as given in Fig. 1.[11] Even in this case, our conclusion would change only quantitatively, not qualitatively.

III. RESULTS AND ANALYSIS

We measured the temperature dependence of the magnetization of $ZnCr_2O_4$ from 300 to 2 K at four different fields for each of four pressures (1 bar, 3.5, 7.0, and 9.5 kbar). Figure 1 shows the temperature dependence of the magnetization for a few representative fields and pressures: $H=0.4$ and 5 T for ambient pressure and 9.5 kbar. The solid lines shown in each figure are for fitting results using the quantum tetrahedral mean field theory (QTMFT) model, which will be discussed later on. All the magnetization measurements were carried out after zero field cooling from well above the transition temperature. As shown in Fig. 1, the magnetization follows the Curie–Weiss behavior at high temperature before reaching a maximum at 35 K and then decreases abruptly near the antiferromagnetic transition.[6] Upon further cooling, however, it increases rather slowly. The small increase at very low temperatures, we think, is due to an unreacted Cr_2O_3 impurity. With increasing magnetic fields, the overall shape of the magnetization does not change much in the paramagnetic phase while the drop below the maximum becomes noticeably smaller. On the other hand, one observable effect of pressure in Fig. 1 is that the fall below the maximum gets larger with increasing pressure as shown in Figs. 1(c) and 1(d).

In order to investigate the field and pressure dependence of the transition temperature and its associated gap energy, we have measured the temperature dependence of the magnetization in further detail from 16 to 5 K at twelve different field values for each of five pressures (1 bar, 3.5, 5.0, 7.0, and 9.5 kbar). Figure 2 shows the blown-up picture of the magnetic susceptibilities near the transition temperature taken at a few selected fields for 1 bar and 9.5 kbar, where the slope changes markedly at the transition temperature. With increasing fields from 0.2 to 5.0 T, the susceptibility decreases more slowly. Similarly, the magnetic susceptibility

decreases with increasing pressures too. In order to determine the transition temperature accurately, we have taken the temperature derivative of the susceptibility. As shown in Fig. 2(c), the temperature derivative of the susceptibility taken at 0.4 T and 1 bar shows a distinct peak at 12.8 K, slightly higher than the reported transition temperature of 12.5 K.

With increasing pressures, there are two unmistakable effects of pressure. First, the width of the transition indicated by the peak in the $d\chi/dT$ plot gets significantly broadened with increasing pressure. It is intriguing to remark that perhaps at 9.5 kbar there might well exist another transition at lower temperatures. In order to check if any of the observed broadening may be due to some pressure gradient inside the cell, we have measured the superconducting transition temperature of Sn under the identical conditions to find that the width of T_c is 0.14 K at 9.5 kbar, compared with 0.09 K at ambient pressure. This renders unlikely an explanation that pressure gradients inside the cell are responsible for the increased width, over 2 K, of the transition of $ZnCr_2O_4$ at such high pressures. Our experimental observation then opens up an interesting interpretation. According to a theory[7] the bond order and the spin order develop accidentally at the same temperature in $ZnCr_2O_4$, and under certain conditions the order parameters of each state can, in principle, condense at different temperatures. In the latter case, the bond order is expected to precede the spin order. Therefore, our observation of the broadened peaks in the $d\chi/dT$ may indicate that such a theoretically predicted splitting occurs at high pressures in the transition temperatures of the two order parameters. Second, increasing field apparently suppresses the strength of the transition, i.e., the peak height in the $d\chi/dT$ plot, as shown in Fig. 2(d). For example, the peak height in the $d\chi/dT$ plot of the data taken at 3.5 kbar is reduced by as much as about 70% with increasing fields to 5 T. This may imply that the first order nature of the transition at ambient pressure is considerably weakened with fields. The field and pressure dependence of the transition temperature is summarized in Fig. 3(a). Interestingly, at low pressure the transition temperature increases continuously with magnetic field, and with increasing pressure the low-field transition temperature increases gradually too. On the other hand, the field-induced increase becomes smaller and eventually there is very little field dependence at 9.5 kbar.

A further interesting point is the pressure and field dependence of the spin gap estimated from our susceptibility data. With the gap opening in the spin excitations as observed by the inelastic neutron scattering experiment,[6] it is also naturally reflected in the temperature dependence of the magnetic susceptibility leading to the exponential temperature dependence of the susceptibility below the transition temperature. Thus, the susceptibility has the following formula:

$$\chi(T) = \chi_1 \times e^{-\Delta_E/k_B T} + \chi_0, \tag{1}$$

where Δ_E is the gap energy and χ_0 the magnetic susceptibility value at $T=0$ K. We note that a similar formula was previously used for a $S=\frac{1}{2}$ frustrated spin chain system with a spin gap.[12] As shown in the insets of Figs. 2(a) and 2(b), this equation explains reasonably well the temperature dependence of the susceptibility below T_N. In order to render consistency to our analysis, we kept the same temperature range from 12 to 8 K for all our estimates of the gap energy. Our estimate of the gap energy is $\Delta_E=5.89$ meV at ambient pressure and 0.2 T, while it is $\Delta_E=6.07$ meV at 9.5 kbar and 0.2 T. Although we acknowledge that we used a rather small region of temperature for our fitting because of the unwanted low temperature upturn from the Cr_2O_3 impurity, however, we note that the estimated gap value of 5.89 meV at ambient pressure and low field fares reasonably well with the value of 4.5 meV measured by inelastic neutron scattering.[6] Thus, we believe that our fitting results capture successfully the essential features of what is actually happening in $ZnCr_2O_4$ under pressure and field.

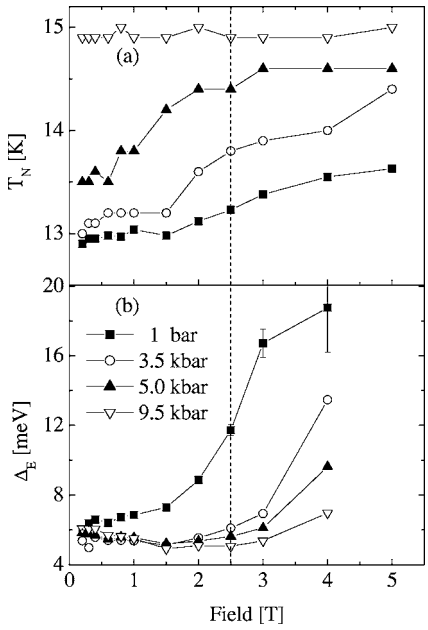

FIG. 3. Field and pressure dependence of (a) the transition temperature and (b) the gap energy, Δ_E. We used the same symbols in both figures. The vertical dashed line indicates where the magnetization shows a field-induced anomaly as shown in Fig. 4.

The summary of our analysis of the gap energy is given in Fig. 3(b). At ambient pressure the gap energy increases gradually at a lower field and then rather rapidly at higher fields. However, this field dependence is quite suppressed with increasing pressures, and eventually the field dependence of the gap energy becomes very weak. We found that we could not determine the gap energy for the 5 T data with reasonably good accuracy, so we do not show them here. Compared with the field and pressure dependence of the transition temperature, the monotonous dependence of the gap energy on pressure and field is rather striking. It is especially interesting that despite the same gap energy estimated for all five pressure values with $H=0.2$ T the actual transition temperature increases by almost 2 K with increasing pressures from 1 bar to 9.5 kbar. Closely related to it, we note that since the peak in the $d\chi/d$T plots gets significantly broadened with increasing pressure it may be misleading to take the maximum of the peak simply as a transition temperature as we discussed above. We propose instead that this disparate field and pressure dependence seen for T_N and Δ_E

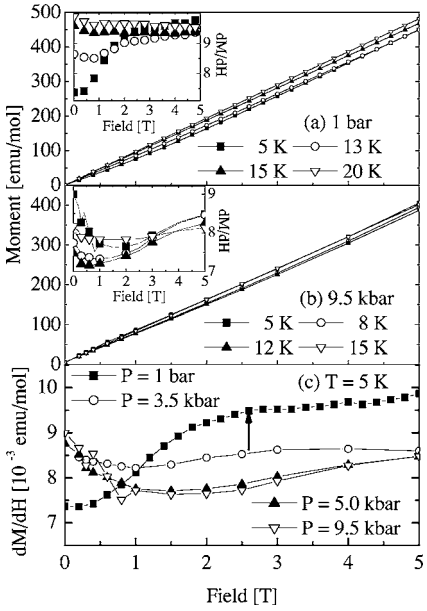

FIG. 4. Field dependence of magnetization at (a) ambient pressure and (b) 9.5 kbar. The insets are for the field derivative of magnetization, dM/dH, at several temperatures. We used the same symbols in the insets for each temperature as in the main figures. (c) Field derivative of the magnetization taken at 5 K for four pressures. The arrow indicates where the metamagnetic transition occurs at 1 bar.

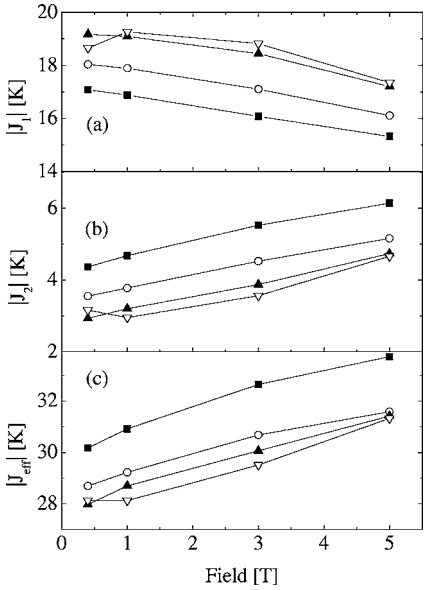

FIG. 5. Pressure and field dependence of (a) J_1, (b) J_2, and (c) $J_{eff}(=J_1+3J_2)$ for 1 bar (filled square), 3.5 kbar (open circle), 7.0 kbar (filled triangle), and 9.5 kbar (open down triangle). J_1 and J_2 were obtained from fitting the data given in Fig. 1 using the QTMFT[13] (see the text).

is likely to be due to an intricate interplay and coupling between the spin and lattice degrees of freedom in $ZnCr_2O_4$.

In addition to the unusual behavior of T_N and Δ_E, there is another interesting point about the magnetic properties. As shown in Fig. 4(a), the magnetization is linear in field and does not show any anomaly above the transition temperature. However, with cooling below T_N the magnetization develops nonlinear field dependence near $H_m=2.5$ T, i.e., a metamagnetic transition, as better shown in the inset of the dM/dH plots. With increasing pressures from 1 bar to 9.5 kbar, the nonlinear field dependence of the magnetization becomes subdued. Similar behavior was observed in the data taken at 5.0 and 7.0 kbar, which were not shown here for the sake of better presentation. (We measured the background signals of the pressure cell without the sample for every setting of pressure and field values, and then subtracted off them from the actual signals taken with the sample inside the cell.) This pressure dependence of the metamagnetic transition is better seen in Fig. 4(c), where we compare dM/dH taken at 5 K for four pressures. As one can see, the anomaly at 2.5 T in the dM/dH plot for 1 bar appears to move toward higher fields with increasing pressures. It is interesting to note that both T_N and Δ_E show some kind of anomaly near $H_m=2.5$ T as shown in Fig. 3, supporting our conclusion that the metamagnetic transition is real and reflects changes to the ground state properties. However since the change in the magnetization data is rather modest we believe that the field-induced transition is of subtle nature.

In order to understand the overall field and pressure dependence of the magnetization and, in particular, how the magnetic ground state of $ZnCr_2O_4$ evolves with pressure and field, we have tried to fit the susceptibility data taken from 5 to 300 K using the quantum tetrahedral mean field theory (QTMFT) proposed by Huber *et al.*[13] A few selected fitting results are shown together with the raw data in Fig. 1. As one can see in Fig. 1, the model describes successfully the susceptibility over wide temperature, field, and pressure ranges. From this fitting procedure, we can obtain two interaction terms, J_1 and J_2. J_1 is an interaction term between nearest spins belong to the same tetrahedron, and J_2 represents the next-nearest-neighbor interaction. In order to check the validity of our results taken using the pressure cell, we have independently measured the magnetization at ambient pressure without the pressure cell. From this comparison of the two data sets taken with the same field at ambient pressure, we could make sure that our J_1 and J_2 values obtained using the data taken with the pressure cell agree with those obtained from the data taken without it. For example, the ambient pressure data taken with the pressure cell give $J_1=-17.8$ K and $J_2=-4.4$ K while the data taken without the pressure cell produce $J_1=-16.6$ K and $J_2=-2.9$ K; the previous report[13] gives $J_1=-19.2$ K and $J_2=-2.3$ K for low field and ambient pressure. Therefore, we can be sure that our analysis is consistent with the previous results and our data taken using the pressure cell are free of any unwanted effects of the pressure cell, at least qualitatively. We stress that this model has not yet been tested for as wide a field and pressure ranges as we have done here. The summary of our fitting results are given in Fig. 5; magnetic field decreases (increases) J_1 (J_2) while pressure increases (decreases) J_1 (J_2). The resulting total effective coupling $J_{eff}(=J_1+3J_2)$ decreases with pressure while it increases with fields as shown in Fig. 5(c). Prior to further discussion, we caution that our estimates of J values may be affected quantitatively, but not qualitatively, by the temperature-induced pressure

drop inside the pressure cell while cooling from room temperature to low temperatures as we discussed in the experimental section.

This observed pressure and field dependence of J_1 and J_2 can be understood in the following manner. First, the pressure dependence of J_1 is natural as the nearest neighbor interaction would increase once the bond distance is reduced with pressures. In particular, the exchange interaction J is expected to vary exponentially with a Cr-Cr distance.[14] The field dependence of both J_1 and J_2 can be understood through a collinear model of the magnetic structure, which is theoretically shown to be one of several possible magnetic structures for $ZnCr_2O_4$.[15] For this collinear model and under the assumption that all the spin moments point along the z axis, then it can be easily shown that a variation in the total energy is given by $\Delta U = 2S^2 (\Delta J_2 - \Delta J_1)$ to the leading order up to the next-nearest neighbors, where S denotes the spin value of Cr ions. Therefore, the observed field dependence of both J_1 and J_2 lowers the total energy. Please note that both J_1 and J_2 are negative values. It may appear to be surprising that although both J_1 and J_2 are of antiferromagnetic nature the observed different field dependence equally lowers the total energy. This apparently self-contradicting results arises from the collinear magnetic ground state of $ZnCr_2O_4$, which is the direct result of the spin-lattice coupling.[7]

IV. SUMMARY

To summarize, we found that there is a subtle, but clear field-induced transition around 2.5 T at which the magnetization shows a deviation from the low-field linear behavior. That our T_N and Δ_E show similarly clear anomalies at a similar field value reinforces our forgone conclusion on the field-induced transition. The nature of the transition, however, is still unclear although we speculate that the high field state arises from a delicate change to the ground state as there is no drastic change in the total magnetization value as a function of fields. Another important experimental observation is the broadening of the peak in $d\chi/dT$ as shown in Fig. 2(c). A possible explanation of the broadening is that with increasing pressure and possibly field, the bond order and the spin order may condense at different temperatures with the former preceding the latter. This kind of splitting in the transitions of the two order parameters were found to be a theoretically stable solution.[7] This conclusion can be tested using a polarized neutron diffraction experiment. We have also shown that the field and pressure dependence of the magnetization can be understood in terms of the QTMFT model. The field and pressure dependence of J_1 and J_2 can be rationalized, at least qualitatively using the collinear Néel state.

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[15] Here we assumed a collinear magnetic model as depicted in Fig. 1(b) in recent studies (Ref. 14). We note that this collinear model is found to be one of several possible magnetic structures for $ZnCr_2O_4$ by a recent theory (Ref. 7).