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Field-Induced Structural Transition in the Bond Frustrated Spinel $ZnCr_2Se_4$ *

CHEN Xu-Liang(陈绪亮)[1,2], SONG Wen-Hai(宋文海)[1], YANG Zhao-Rong(杨昭荣)[1,2,3]**

[1]*Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031*
[2]*High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei 230031*
[3]*Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093*

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The effect of an external magnetic field on the structural and magnetic properties of bond frustrated $ZnCr_2Se_4$ at low temperatures is investigated using magnetization, dielectric constants and thermal conductivity experiments. With an increase in the magnetic field H, the antiferromagnetic transition temperature T_N is observed to shift progressively toward lower temperatures. The corresponding high temperature cubic ($Fd\bar{3}m$) to low temperature tetragonal ($I4_1amd$) structural transition is tuned simultaneously due to the inherent strong spin-lattice coupling. In the antiferromagnetic phase, an anomaly at H_{C2} defined as a steep downward peak in the derivative of the M–H curve is clearly drawn. It is found that T_N versus H and H_{C2} versus T exhibit a consistent tendency, indicative of a field-induced tetragonal ($I4_1amd$) to cubic ($Fd\bar{3}m$) structural transition. The transition is further substantiated by the field-dependent dielectric constant and thermal conductivity measurements. We modify the T–H phase diagram, highlighting the coexistence of the paramagnetic state and ferromagnetic clusters between 100 K and T_N.

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Chromium spinels with the formula ACr_2X_4 (where A=Zn, Cd, Hg and X=Se, S or O) host a chain of corner-sharing tetrahedra known as the pyrochlore sublattice. This topology features one of the most highly frustrated networks when the neighboring magnetic Cr^{3+} ions interact antiferromagnetically since geometric and/or bond frustrations may become involved. Frustration dependent on the separation of Cr^{3+} ions is the leading driving-force behind many novel phenomena. For instance, in $ZnCr_2O_4$, a Peierls-like structural transition was unveiled along with a release of geometric frustration.[1,2] For chalcogenide spinels, bond frustration related splitting of phonon modes was clearly observed in the infrared spectrum.[3,4] These anomalies cast a light on the importance of spin-phonon coupling since the Cr^{3+} ions in an octahedral crystal field are Jahn–Teller inactive, which results in a quenching of the orbit and charge degrees of freedom.

Application of an external magnetic field favors the ferromagnetic correlation and thus may lift frustration, at least partially. For example, novel fractional magnetization states were observed universally for Cr-based oxide spinels.[5−7] However, the physics behind this phenomenon remains ambiguous since the required field is very high and is not easily accessible for experimental investigations. Recently, important progress was made where researchers used neutron and x-ray diffraction techniques under high magnetic fields to study $HgCr_2O_4$.[7] Their results showed that spin-lattice coupling plays a significant role in stabilizing the field-induced states. Such transitions challenge the traditional understanding of magnetism because they refer to not only strong spin correlations but also associated distortions of lattice symmetries.[8] In particular, for $ZnCr_2Se_4$, the infrared spectrum exhibited a splitting of the lowest mode accompanied by the antiferromagnetic transition.[4] A strong spin-lattice coupling effect was also observed in ultrasound experiments under a magnetic field, where sound velocity shows a plateau behavior above 7 T at 2 K, implying a possible magneto-structural transition.[9] Plumier investigated the low-field states via neutron diffraction and observed a reorientation of the magnetic domains without any change of structural symmetry.[10] Due to a lack of x-ray and neutron data under a high field, the question whether there is an existence of a field-induced structural transition in $ZnCr_2Se_4$ remains unclear and merits further investigation.

In this Letter, the effects of an external magnetic field on the structure and magnetic symmetries below the Néel temperature T_N in bond frustrated $ZnCr_2Se_4$ have been studied. The finding that T_N–H and H_{C2}–T show exactly the same characteristics convinces us that a field-induced structural transition occurs near 70 kOe starting from 2 K as suggested in Ref. [9]. Dielectric and thermal conductivity under different fields further substantiates our conclusions. We construct the H–T phase diagram, with special attention on the temperature region near T_N.

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**Corresponding author. Email: zryang@issp.ac.cn

Details about the sample preparation procedures and sample structural and magnetic characterizations can be found elsewhere.[11] The specific heat and thermal conductivity results were obtained from a quantum design physical property measurement system (PPMS). Dielectric measurements were performed by using an LCR meter (TH2828S) integrated to a SQUID with the electric field applied perpendicular to the magnetic field direction.

The magnetization $M(T)$ as a function of temperature under different external magnetic fields is presented in Fig. 1. Here $M(T)$ exhibits a sharp downturn followed by a continuous gradual decrease down to lower temperatures. The downturn marked as T_N signals the antiferromagnetic transition.[12] This coincides with the fact that the lattice structure is cubic at high temperature, while then undergoing a phase transition into the tetragonal structure below T_N at zero field.[11,13,14] With an increase in the magnetic field, T_N is shifted systematically to lower temperatures. The magnetic and structural transitions appear to occur at the same temperature due to the strong spin-lattice coupling.[11,15] Hence, the antiferromagnetic order is moved under fields and the corresponding structural transition should be shifted simultaneously.

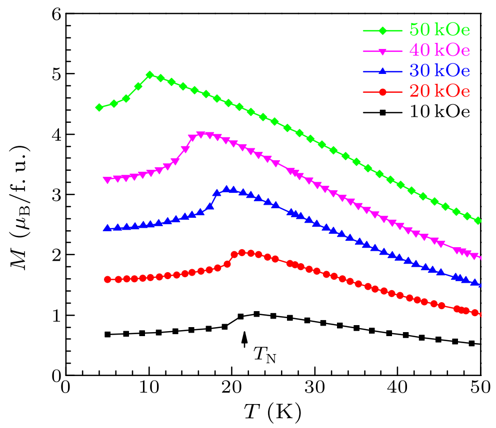

Fig. 1. (Color online) Low temperature dependence of the magnetization M for a polycrystalline sample $ZnCr_2Se_4$ at different external magnetic fields.

The field dependent magnetization $M(H)$ at 5 K is shown in Fig. 2(a). With an increase in the field, $M(H)$ first increases continuously followed by a kink at about H_{C1} = 15 kOe. Here H_{C1} is related to the reorientation of inequivalent domains due to a tetragonal structure below T_N.[10] At the same time, tilting of the spin rotation axes occurs, making the spins evolve from helical to conical spin configurations. Beyond H_{C1}, $M(H)$ increases almost linearly with a larger slope and the conical angle becomes continually smaller. Another anomaly is observed at about H_f = 65 kOe. This should correspond to a transition related to an unsaturated meta-stable ferromagnetic state due to the fact that $ZnCr_2Se_4$ resembles to possess a completely ferromagnetic alignment until H_S = 100 kOe as indicated by the red dashed line in Fig. 2(a), in agreement with the previous investigation.[9]

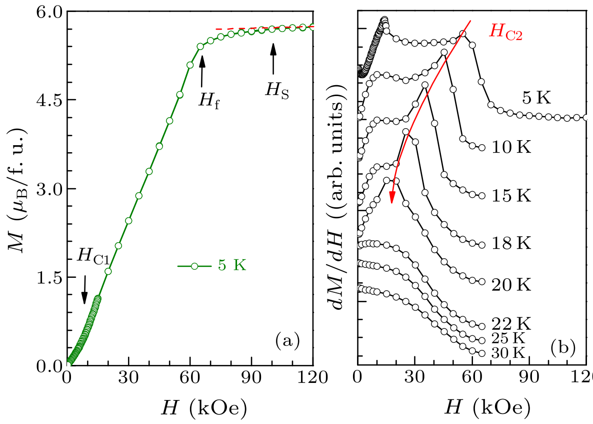

Fig. 2. (Color online) (a) The value of M versus H at 5 K with the critical fields H_{C1} and H_f marked. (b) The derivative of M with respect to H at temperatures below and above T_N, where the critical field H_{C2} is indicated in red arrow.

Both the present M–H curve and the curve in Ref. [9] exhibit three anomalies up to 120 kOe below T_N. However, we note that the field of the second anomaly at H_f is somewhat higher than the value at H_{C2} in Ref. [9] for the same temperature. As a result, H_f is not the same anomaly as observed in H_{C2} in Ref. [9]. This observation triggered us to process the data more carefully. Indeed, another anomaly at H_{C2} ~55 kOe at 5 K was found from the derivative of the M–H curve and the values coincide with that of H_{C2} at 5 K in Ref. [9]. This coincidence leads us to consider that the anomaly at H_{C2} is of the same origin as that in Ref. [9], most likely a field-induced structural transition.

Upon warming, we find that H_{C2} becomes continually smaller for other selected temperatures below T_N and vanishes above T_N, as plotted in Fig. 2(b). We tentatively plot T_N versus H (solid squares) and H_{C2} versus T (solid right-angles) together in Fig. 4 and find a consistent tendency between them as indicated by the red line. Therefore, the anomaly at H_{C2} should be assigned to a field-induced structural transition. This observation is further substantiated by the following field-related measurements.

Specific heat is displayed in the representation of C/T versus T in Fig. 3(a). A very sharp peak is observed at T_N, in agreement with the previous result.[15] The sharp nature of this peak indicates that it is a first-order type transition. The phonon contribution to the entropy decreases continuously with temperature and is indicated by the red line in the inset of Fig. 3(a). The magnetic entropy involved in the transition is the area under the peak anomaly and can be estimated via $\Delta S = \int (C - C_{\rm phonon})/TdT$, where C and $C_{\rm phonon}$ denote the total specific heat and phonon component, respectively. The value of ΔS is 2.65 J·mol^{-1}K^{-1}, reaching about 11.5% of the full entropy ($2R\ln 4$) expected for the well-aligned Cr spins. This anomaly of low spin entropy suggests that a large amount of entropy was already released at a temperature far above $T_{\rm N}$ since ferromagnetic fluctuations have been reported at a temperature as high as 100 K where ferromagnetic clusters gradually grow in size upon cooling.[11]

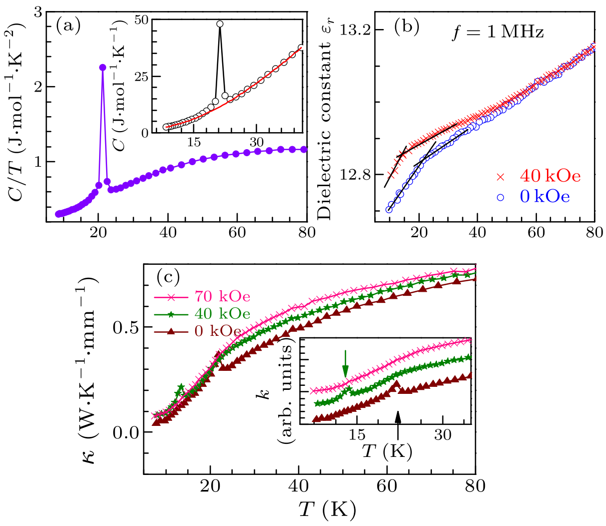

Fig. 3. (Color online) (a) Temperature dependence of the specific heat plotted as C/T versus T. Inset: a polynomial fitting of the phonon specific heat. (b) The relative dielectric constant $\varepsilon_{\rm r}$ versus T for $f = 1000$ kHz at $H = 0$ and 40 kOe. (c) Low temperature dependent thermal conductivity κ at 0 kOe, 40 kOe and 70 kOe. Inset: a detailed draw in the vicinity of phase transition. For clarity, the curves are translated vertically and the anomalies are labeled by different colored arrows.

The dielectric constants $\varepsilon_{\rm r}$ at zero field and 40 kOe at a frequency of $f = 1000$ kHz are shown in Fig. 3(b). The magnitude of $\varepsilon_{\rm r}$ does not vary much with frequency (not shown here). As the temperature drops, $\varepsilon_{\rm r}$ decreases almost linearly. On approaching $T_{\rm N}$, a kink followed by a constant downturn is observed. The critical temperature at the anomaly coincides with $T_{\rm N}$ and should be related to the associated structural transition, as also evidenced by the above specific heat data. The anomaly can be tuned to ∼14 K under a field of 40 kOe in addition to an increase of $\varepsilon_{\rm r}$. The phase line boundary of $T_{\rm N}$ in the temperature-field space is shown by a red line in Fig. 4. From this, it can be seen that the magnetic and lattice degrees of freedom are intimately coupled and an external magnetic field can shift the structural transition to a lower temperature due to its inherent strong spin-lattice coupling, proving a spin origin of the structural transition. This conclusion also agrees with the following thermal conductivity measurements.

Thermal conductivity κ as a function of temperature at 0 kOe, 40 kOe and 70 kOe are shown in Fig. 3(c). At zero field, κ decreases constantly as the temperature drops, until $T_{\rm N}$, where a cusp appears followed by a decrease again down to the lowest temperature. The traditional phonon thermal conductivity first increases and reaches a broad maximum, then decreases rapidly upon cooling where it can be modeled as $\kappa = \frac{1}{3}C_v lv$, where C_v is the specific heat, l is the mean free path, and v is the averaged phonon velocity that does not vary much with temperature.[16] With a decreasing temperature, l becomes constantly larger due to the reduction of the number of short-wave phonons that scatter the thermal carriers. This results in the initial increase of κ. When the size of l is comparable with the dimension of the sample, κ reaches a maximum. Upon further cooling, the scattering of the thermal carriers is dominated by impurities and defects. In this case, κ is proportional to the specific heat C_v, resulting in a rapid decrease at low temperatures.

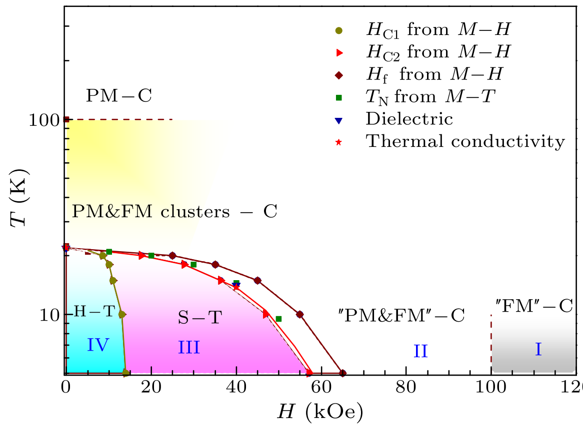

Fig. 4. (Color online) The T–H phase diagram of $ZnCr_2Se_4$. Here H and S stand for helical and spiral spin configurations; PM and FM denote paramagnetic and ferromagnetic states; T and C correspond to tetragonal ($I4_1amd$) and cubic ($Fd\bar{3}m$) lattice structures, respectively.

As can be seen from Fig. 3(c), κ did not exhibit a broad peak at zero field. It has been proven that phonons can be scattered by spins.[17] Considering that the spin and lattice degrees of freedom are coupled to each other, the suppression of the broad phonon thermal conductivity peak implies that strong spin fluctuations are present, which is also in accordance with the specific heat data. The observed cusp should be related to the structural transition as a sharp peak is also observed in the specific heat data at the same temperature. When applying a magnetic field of 40 kOe, the cusp approaches 13.8 K. It should be noted that this characteristic point coincides with that of the dielectric result, see Fig. 3(b). Under a field of 70 kOe, the peak anomaly is suppressed completely, indicating a disappearance of the structural transition. Not far above T_N, since the magnetic field inhibits the spin fluctuations, κ reveals an enhancement as observed in Fig. 3(c). The characteristic discontinuities from the specific heat, dielectric and thermal conductivity curves are all located exactly on the red line drawn in Fig. 4, which confirms the existence of the field-induced structural phase transition.

Although an H–T phase diagram has been previously investigated,[9] we revisit it here by emphasizing the finding of a new magnetic phase between 100 K and T_N. Through a previous study,[11] we identified a state containing FM clusters and paramagnetism (PM) coexisting between 100 K and T_N. Together with the results of this work, the magnetic phase diagram of $ZnCr_2Se_4$ is shown in Fig. 4. Above 100 K at zero field, the system is paramagnetic with cubic structure symmetry. Upon cooling, some FM clusters appear and coexist with the PM state. The lattice symmetry is still cubic, although NTE arises. Below T_N, an incommensurate helical spin configuration arises with a tetragonal lattice structure. It is the H–T phase, i.e., phase Ⅳ. With the application of a magnetic field, two other phases emerge. The transition from phase Ⅲ to phase Ⅱ is bounded by H_{C1}. In phase Ⅲ, the helical spins develop into a conical spiral (S–T phase). With a further increase in the field, phase Ⅲ transitions into phase Ⅱ and a spin-driven structural transition occurs, which is traced by the H_{C2} anomaly drawn from the derivative of the M–H curve as well as from the dielectric constant and thermal conductivity results. Here H_f signals a thermodynamic change of the ferromagnetic domains without a spin phase transition. In phase Ⅱ, an unsaturated state sets in and the spin configuration may be a mixture of PM and FM with a cubic lattice symmetry, or 'spin nematic'[9] as suggested in the previous study. Finally, a complete spin-polarized state or FM state reaches above H_S, that is, phase I.

In summary, we have investigated the evolution of the magnetic and structural properties with respect to an applied external magnetic field for $ZnCr_2Se_4$. Three distinct phases are identified in different magnetic field regions within the antiferromagnetic phase starting from below T_N. At low fields, an incommensurate phase with helical spin configuration is present. Starting from H_{C1}, the ground state spin configuration forms a conical spiral. After H_{C2}, the system becomes partially paramagnetic while possibly forming ferromagnetic clusters as it crosses the T_N phase boundary line which decreases in temperature with an increase in the field, where a magnetostructural transition occurs. The transition is further substantiated by the field dependent dielectric constant and thermal conductivity measurements. Above H_S, a fully aligned ferromagnetic state sets in. A complete T–H phase diagram is constructed, with special attention paid to the temperature region near T_N where a coexisting phase of PM and FM clusters occurs.

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