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Study of negative thermal expansion in the frustrated spinel $ZnCr_2Se_4$

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The origin of negative thermal expansion (NTE) in the bond frustrated $ZnCr_2Se_4$ has been explored. ESR and FTIR document an ideal paramagnetic state above 100 K, below which ferromagnetic clusters coexist with the paramagnetic state down to T_N. By fitting the inverse susceptibility above 100 K using a modified paramagnetic Curie-Weiss law, an exponentially changeable exchange integral J is deduced. In the case of the variable J, magnetic exchange and lattice elastic energy couple with each other effectively via magnetoelastic interaction in the ferromagnetic clusters, where NTE occurs at a loss of exchange energy while a gain of lattice elastic one. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4867217]

I. INTRODUCTION

Magnetic frustrated systems have recently been a subject of continuing interests for a manifold of fascinating states, such as spin ice, spin liquid, and orbital glass, may be surviving down to $T = 0$.[1–3] Among the reported materials, chromium-based spinels with the formula ACr_2X_4 (X = O, S, and Se) are of essential role not only of being theoretical interests but also in exploring potential multi-functional materials.[4–7] For instance, magnetoelectric effect or multiferroicity is observed in $ZnCr_2Se_4$.[8,9] In addition, it allows the adjustments of the direction and magnitude of electric polarization via applied magnetic field.[9] The design or tuning of multi-functional materials for potential applications enables the necessity to clear what stands behind the novel phenomena observed.

$ZnCr_2Se_4$ with negative thermal expansion (NTE) is a case in point.[6,10] This compound exhibits a large positive Curie-Weiss temperature.[11] However, neutron diffraction study revealed at $T_N = 21$ K a complex helical spins consisted of ferromagnetic (FM) layers along [001] with a turning angle of 42° between the adjacent ones.[12–14] While early X-ray diffraction (XRD) and neutron powder diffraction indicated a tetragonal structural transformation at T_N, subsequent neutron and synchrotron radiation results on single crystal showed an orthorhombic phase.[13–15] Moreover, recent neutron powder diffraction found no sign of structural transition.[10] In fact, the exact lattice symmetry is still subject of debate. On the other hand, IR spectroscopy experiment reported a marked splitting of the low-frequency mode below T_N.[16] This elucidates an essential spin-phonon coupling. Both geometrical and additional bond frustration are believed to be crucial factors.[6,17] In addition, since Cr^{3+} in an octahedral crystal field is Jahn-Teller inactive, spin-phonon coupling is of vital importance in lifting frustration. Moreover, the correlation between spin and lattice degrees of freedom is also revealed by the recent ultrasonic experiments.[18] Nevertheless, the very origin of NTE is yet far from being well understood.

In the present paper, a set of experimental techniques is utilized to probe the spin-lattice correlation in $ZnCr_2Se_4$. By considering a variable exchange integral J with respect to temperature or lattice constant, NTE is attributed to a result of the competition between magnetic exchange and lattice elastic energy via magnetoelastic coupling.

II. EXPERIMENTS

The polycrystalline sample of $ZnCr_2Se_4$ was prepared by standard solid state reaction method. High purity powders of zinc (99.9%), chromium (99.9%), and selenium (99.9%) were mixed according to the stoichiometric ratio. Next, the powders were sealed in an evacuated quartz tube and heated slowly to 850 °C in seven days. Then the sample was reground, pelletized, sealed, and heated again for another three days at 850 °C. The magnetic data were collected on a Quantum Design superconducting quantum interference device (SQUID) magnetometer. The temperature dependent XRD patterns were obtained using XRD (Rigaku TTRIII). ESR measurements were performed using a Bruker EMX plus 10/12 CW-spectrometer at X-band frequencies ($\upsilon = 9.39$ GHz) in a continuous He gas-flow cryostat for 2–300 K. The transmittance spectra were collected in the far-infrared range using the Bruker Fourier-transform spectrometer Vertex 80v equipped with a He bath for 5–300 K.

III. RESULTS AND DISCUSSION

The XRD data were analyzed using the standard Rietveld technique, which shows a single-phase material with cubic spinel structure at room temperature. Figure 1(a) shows the temperature (T) dependence of lattice constant a. With decreasing temperature, a first decreases rapidly and then manifests a negative thermal expansion behavior below about $T_E = 60$ K, which is almost concordant with the previous results.[6,10] Upon further cooling below 20 K, splitting of

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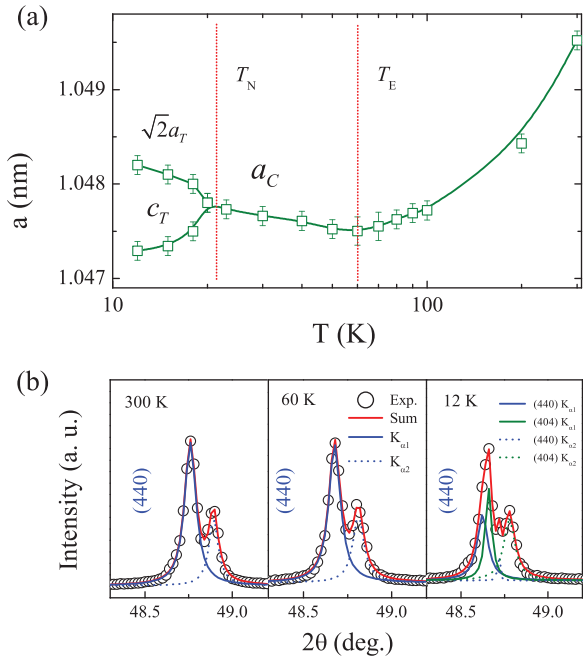

FIG. 1. (a) Temperature dependent lattice parameter a vs T in semilogarithmic for $ZnCr_2Se_4$. Error bars are average of repeated fittings. The negative thermal expansion initial temperature T_E and the antiferromagnetic order one T_N are drawn in red doted lines. (b) The representative peaks (440) at 300 K, 60 K, and 12 K. Circles are experimental data; Solid and dashed lines are Lorentzian fits.

several peaks in XRD spectra are observed. The representative peak (440) at 12 K that splits into (440) and (404) is presented in Fig. 1(b). This signals a cubic to tetragonal structural transition with space group $I4_1/amd$.[13,15]

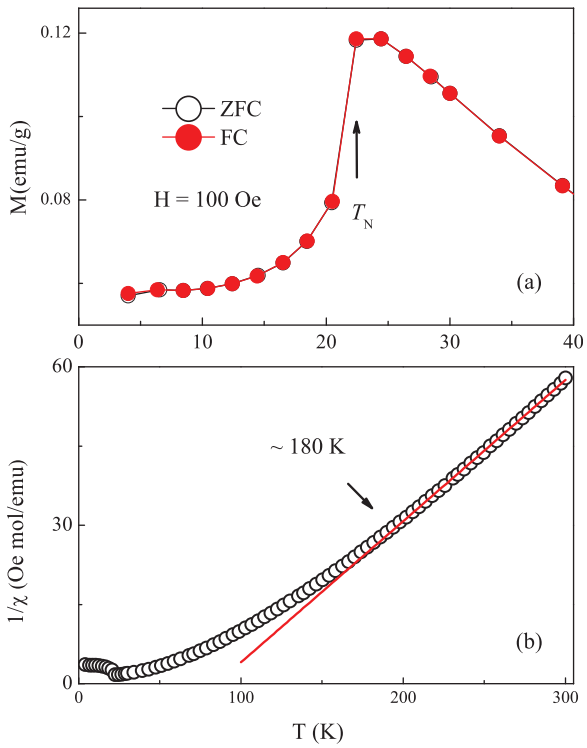

FIG. 2. (a) Low temperature dependence of the magnetization M for a polycrystalline sample $ZnCr_2Se_4$ at 100 Oe. (b) A Curie-Weiss fitting of the inverse susceptibility.

Figure 2(a) presents the magnetization (M) versus T at low applied magnetic field of 100 Oe under both zero-field-cooled (ZFC) and field-cooled (FC) sequences. At about $T_N = 22$ K, M shows a sharp antiferromagnetic (AFM) transition.[6,10,12–14] Figure 2(b) shows a fitting of the inverse susceptibility $1/\chi$ according to the paramagnetic (PM) Curie-Weiss law $\frac{1}{\chi} = \frac{T-\Theta_{CW0}}{C}$. A large positive Curie-Weiss temperature $\Theta_{CW0} = 85$ K and the coefficient $C = 3.74$ are obtained. The effective magnetic moment calculated by the formula $\mu_{eff} = 2.83\sqrt{C/2}$ (in cgs units) equals to 3.87 μ_B, in agreement with the spin-only Cr^{3+} ion.

The large positive Curie-Weiss temperature implies a dominant FM exchange interaction; however, the compound shows an AFM ordering at low temperatures. Hence, we first investigate the lattice dynamic inspired by the strong spin-lattice correlation. Within the wave-number range inspected, three infrared modes, labeled as *I*, *II*, and *III* are observed simultaneously. Generally speaking, the phonon eigenfrequency follows an anharmonic behavior, which can be described by the following formula:

$$\omega_i = \omega_{0i}\left[1 - \frac{\alpha_i}{\exp(\Theta/T) - 1}\right], \quad (1)$$

where ω_{0i}, α_i, and Θ are the eigenfrequency of mode i with decoupling of the spin and phonon at 0 K, the weight factor of mode i, and the Debye temperature $\Theta = 309$ K.[16] A detailed temperature dependence of eigenfrequency is exhibited in Fig. 3. The solid line is a fitting of classical anharmonic behavior according to Eq. (1). Mode *I* shows negative shifts below T_E and Mode *II* shows positive shifts from about 100 K compared to the normal anharmonic behaviors, respectively. According to Lutz and Zwinscher, the highest

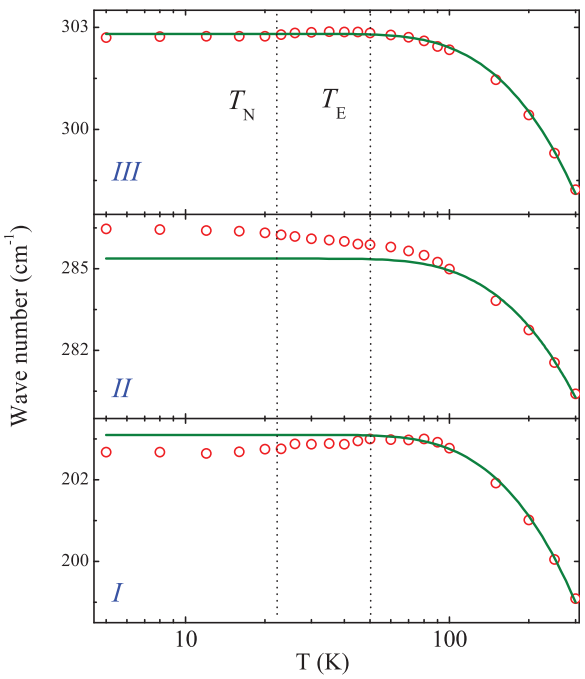

FIG. 3. Temperature dependence of wave number of the infrared activated mode *I*, *II*, and *III* for $ZnCr_2Se_4$. The solid curve is a fit described in the text. The characteristic temperatures are indicated.

frequency mode III is ascribed to the Cr-Se vibration, however, modes II and I originate from combined vibrations of Cr-Se and Zn-Se. For mode II, the ratio of contribution from Cr-Se and Zn-Se is 78:18, while for mode I the ratio of Cr-Se to Zn-Se is 21:73.[19] Cr-Se bond relates to the FM spin super-exchange interaction and Zn-Se links to the AFM super-exchanges.[4] As a result, FM Cr-X-Cr bonds dominate modes II and III while AFM linkages Cr-X-A-X-Cr determine mainly the eigenfrequency of mode I.[20,21] The deviation of mode II below 100 K due to spin-phonon coupling indicates that FM fluctuations involve already at this temperature. Furthermore, the opposite shifts of modes I and II in the NTE temperature region may refer to a dynamic competition of FM and AFM superexchanges.

The temperature dependent ESR spectrum is further investigated. A PM signal is observed at room temperature and it vanishes below T_N (not drawn). The resonant field (H_{res}) and peak-to-peak line-width (ΔH_{PP}) as a function of temperature are plotted in Figs. 4(a) and 4(b), respectively. A typical ESR spectrum at 100 K and fitting using the first-order derivative symmetric Lorentzian function are presented in the inset of Fig. 4(a). As can be seen from Fig. 4(a), with decreasing temperature from 300 K to 100 K, H_{res} shows a constant value while ΔH_{PP} decreases almost linearly. Upon further cooling, H_{res} drops drastically and accordingly ΔH_{PP} broadens greatly, in accordance with Ref. 6.

The g factor is 1.996, in agreement well with the previous works.[6,22,23] The linear decrease of ΔH_{PP} with temperature can be attributed to a single-phonon spin-lattice relaxation mechanism.[24,25] Both the constant g-factor and linear behavior of ΔH_{PP} evidence a well-defined PM state at least above 100 K. Note that H_{res} starts to decrease and ΔH_{PP} broadens at 100 K. Meanwhile, an FM-related positive shift for Mode II is observed in the IR modes in Fig. 3. These can thereby be correlated to the onset of FM fluctuations and spin-phonon coupling. As we know, H_{res} is a sum of H_{int} and H_{ext}, where H_{int} and H_{ext} are the equivalent internal and the external actual fields, respectively. For the case $H_{int} > 0$, the internal field may shift the resonance line to lower field; on the contrary, the resonance signal would appear at higher field with negative internal magnetic field. The decreasing of H_{res} below 100 K indicates an increasing of H_{int}, which may be caused by the interaction between the localized magnetic moments and the demagnetization effect.[24] Therefore, the enhancement of H_{int} and onset of FM fluctuations reveal gradually growing FM clusters, forming an FM-cluster and PM mixed state from 100 K to T_N. The existence of FM clusters is also supported by the following NTE analysis. Below T_N, the signal disappears due to the AFM ordering transition.

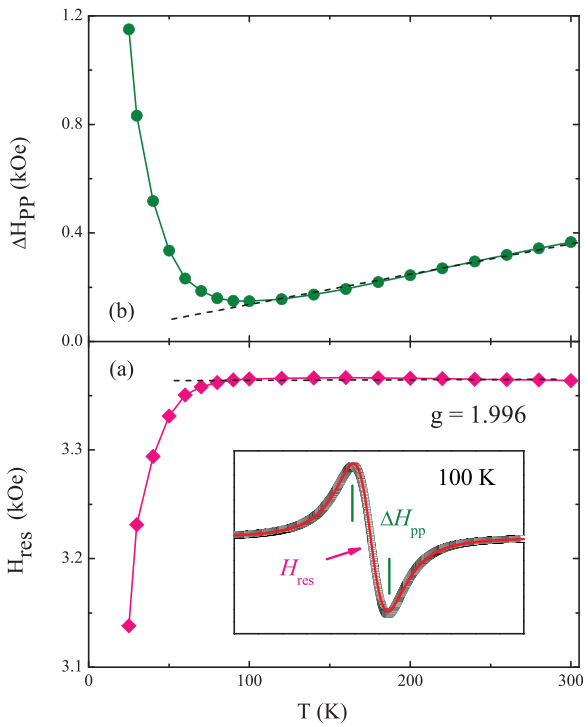

FIG. 4. (a) Temperature dependence of the resonance field H_{res}. Inset: a typical fitting of the ESR spectrum at 100 K, where the definitions of the parameters are shown. (b) The peak-to-peak linewidth ΔH_{PP} vs T. The dashed lines are guided by eyes.

As is discussed above, the system keeps a pure PM state at least above 100 K, so the inverse susceptibility should be described by the PM Curie-Weiss law down to this temperature. However, it departs from the linear behavior at a temperature as high as about 180 K, see Fig. 2(b). Recalling the fitting process in Fig. 2(b), we have assumed a constant Curie-Weiss temperature Θ_{CW0}, i.e., a constant magnetic exchange interaction J. The behavior of IR modes below 100 K implies a competition of FM and AFM superexchange interactions. In addition, the nearest neighbor FM Cr-Se-Cr and other neighbor AFM Cr-Se-Zn-Se-Cr superexchange interactions depend strongly on the lattice constant.[4] It means that the total J may change since a decreases dramatically upon cooling [Fig. 1(a)]. Accordingly, the traditional Curie-Weiss behavior should be modified within the present case to bridge the gap mentioned above. In specific, one should take a variable Θ_{CW} (or J) as a function of T or a into account.

In AFM spinel oxides, the Curie-Weiss temperature changes exponentially with the lattice parameter.[20] Naturally, an empirical description of $\Theta_{CW}(T) = \Theta_{CW0} - \alpha \times e^{-T/\beta}$ is postulated. The fitting of the inverse susceptibility above 100 K using the modified Curie-Weiss behavior $\frac{1}{\chi} = \frac{T-\Theta_{CW}(T)}{C}$ is exhibited in Fig. 5(a). The parameters are $\alpha = 226$ and $\beta = 45$. Furthermore, a remarkable deviation below 100 K in blue short dashed line indicates the appearance of the effective internal field originating from FM clusters. Next, based on the obtained α and β, Θ_{CW} (T) is extrapolated to low temperatures as exhibited in Fig. 5(b). It shows a derivation at about 180 K from the nearly constant value. With further lowering temperature, it decreases faster and faster and below $T \approx 45$ K, Θ_{CW} (T) even becomes negative. These features may interpret qualitatively the fact that $ZnCr_2Se_4$ is dominated by ferromagnetic exchange interaction but orders antiferromagnetically at low temperatures. Since the exchange integral and the Curie-Weiss temperature are linked by $J(T) \propto \Theta_{CW}(T)$ $[J(a) \propto \Theta_{CW}(a)]$, we will use $J(T)$ $[J(a)]$ instead in the following discussion.

Given that J is changeable, magnetic exchange and lattice elastic energies can link effectively with each other via

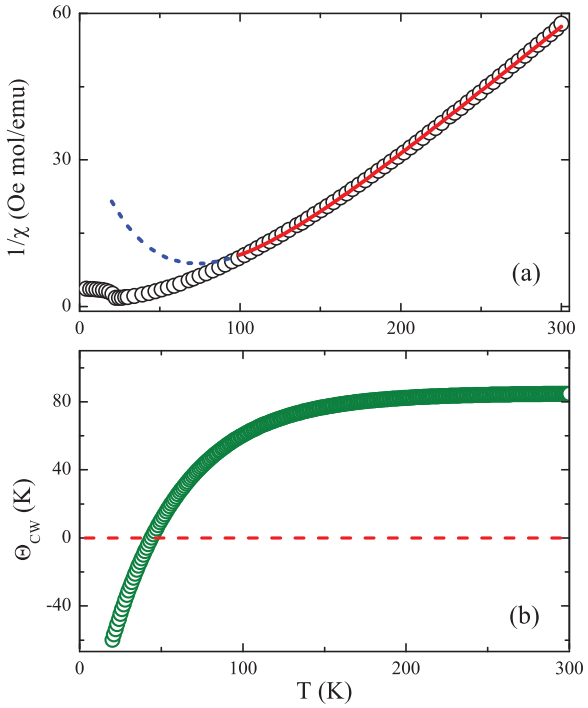

FIG. 5. (a) A fitting of the inverse susceptibility above 100 K in red solid line using $\frac{1}{\chi} = \frac{T-\Theta_{CW}(T)}{C}$ taking a temperature or lattice constant a dependent Curie-Weiss temperature into account. The short dashed blue line is an extension of the fitting to low temperatures. (b) Θ_{CW} vs T and the red dashed line indicates $\Theta_{CW} = 0$ at 45 K.

magnetoelastic coupling. The free energy F in a magnetoelastic system is expressed as

$$F(T) = -J(T)\sum_{i,j}\vec{S}_i \cdot \vec{S}_j + \frac{1}{2}N\omega^2\triangle^2(T) - T \cdot S(T), \quad (2)$$

where N is the number of the ion sites, ω is the averaged vibrational angular frequency, and $\triangle$ is the averaged strain relative to the equilibrium lattice constant. The first term is exchange energy (E_{ex}) as a function of J, the second is lattice elastic energy (E_{el}) related mainly to the lattice parameter a (or equivalent T), and the last is the entropy. From the above equation, we know that if the system stays at an ideal PM state, then $E_{ex} = 0$. So E_{ex} and E_{el} will show no coupling, as is observed from the IR spectra above 100 K.

When the system stays at an FM state with a changeable J, there may exist a competition between E_{ex} and E_{el} since the former is negative while the latter always positive. Indeed, it has been concluded above that J decreases exponentially [Fig. 5(a)] and some FM clusters forms gradually below 100 K. Therefore, the concomitant decrease of J and a causes an increasing E_{ex} but decreasing E_{el} in the FM clusters. At some critical point, a totally compensation between them may present. If a further decreases as cooling, the variation of E_{ex} would gradually exceed that of E_{el} in magnitude. Especially when J drops sharply with respect to a, say here at T_E, a tiny decrement of a will give rise to a dramatic increment of E_{ex} whereas E_{el} keeps nearly constant. The state in a system subjected to stimuli, such as cooling, always tends to develop towards one that can lower F. In this sense it is favorable to lowering F by expanding the lattice parameter a to increase J ($J > 0$), and thereby to decrease E_{ex} due to its negative value, at the same time at a cost of few increases of E_{el} in magnitude. This means that a negative thermal expansion of the lattice originating from the FM clusters with an exponentially changeable J is expected. It is worthy of noting that when applying a magnetic field to the system in the NTE temperature region, NTE in magnitude enhances.[6] This is because the size or population of the FM clusters increases when applying a magnetic field.

On the contrary, when an AFM ordering appears, J becomes negative and the condition to stimulate NTE is not met any more. Normal thermal expansion upon cooling results in a simultaneous decreasing of E_{ex} and E_{el}, which is consistent to lowering F. In fact, a normal expansion feature is observed below T_N.[6] It should be noted that the existence of NTE[6,10] evidences in turn that J is changeable. If J keeps constant in a FM cluster, E_{ex} will be almost constant and a normal thermal expansion of the lattice alone can give rise to a decrease of E_{el} and of F sufficiently.

IV. CONCLUSIONS

To summarize, we have investigated the origin of NTE in strongly bond frustrated $ZnCr_2Se_4$. By fitting the inverse susceptibility above 100 K, an exponentially variable exchange J is deduced. The exchange and lattice elastic energy can effectively couple with each other via magnetoelastic on basis of this changeable J. NTE is qualitatively interpreted as a competition between the two kinds of energy.

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