Spin-driven Phonon Splitting in Bond-frustrated ZnCr₂S₄

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Utilizing magnetic susceptibility, specific heat, thermal expansion and IR spectroscopy we provide experimental evidence that the two subsequent antiferromagnetic transitions in ZnCr₂S₄ at $T_{N1} = 15$ K and $T_{N2} = 8$ K are accompanied by significant thermal and phonon anomalies. The anomaly at $T_{N2}$ reveals a strong temperature hysteresis typical for a first-order transformation. Due to strong spin-phonon coupling both magnetic phase transitions induce a splitting of phonon modes, where at $T_{N1}$ the high-frequency and at $T_{N2}$ the low-frequency modes split. The anomalies and phonon splitting observed at $T_{N2}$ are strongly suppressed by magnetic field. Regarding the small positive Curie-Weiss temperature $\Theta \approx 8$ K, we argue that this scenario of two different magnetic phases with concomitant different magneto-elastic couplings results from the strong competition of ferromagnetic and antiferromagnetic exchange of equal strength.

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During the last decade the fascinating physics of spinel compounds came into the focus of modern solid-state physics and materials science. The classical and still unsolved nature of the Verwey transition in magnetite, where charge and orbital order compete [1], the formation of heavy fermions in LiV₂O₄ [2], the emergence of self-organized spin loops in ZnCr₂S₄ [3], the observation of colossal magneto-resistance in Cu doped FeCr₂S₄ [4] and of gigantic Kerr rotation in FeCr₂S₄ [5], the existence of an orbital glass state in FeCr₂S₄ [6] and of a spin-orbital liquid in FeSe₂S₄ [7], multiferroic behavior and colossal magneto-capacitive effect in CdCr₂S₄ and HgCr₂S₄ [8], spin dimerization in CuIr₂O₄ [9] and MgTi₂O₄ [10], and the spin-Peierls-like transitions in 3-dimensional solids [11,12] are most representative examples of exotic phenomena and ground states which were found recently in a variety of spinel compounds. The appearance of these fascinating ground states is attributed to the competition of charge, spin and orbital degrees of freedom, which are strongly coupled to the lattice. In addition, both A and B sites in the normal AB₂X₄ spinels are geometrically frustrated. Within the B-sublattice further complexity is emerging due to the competition of nearest neighbor (nn) ferromagnetic (FM) with direct as well as next-nearest neighbor (nnn) antiferromagnetic (AFM) exchange. Hence, depending only on the B-site separation, FM and AFM ground states can be found [11,14], and in some cases FM and AFM exchange interactions are of equal strength leading to strong frustration.

In this letter we present a detailed investigation of ZnCr₂S₄ comparing our results with those observed in other zinc-chromium spinels. In these compounds Cr³⁺ reveals a half-filled t₂g crystal-field ground state with almost zero spin-orbit coupling. Despite the fact that oxide, sulfide, and selenide are governed by different exchange interactions, as indicated by their Curie-Weiss (CW) temperatures, they reveal similar magnetic transition temperatures into AFM states: ZnCr₂O₄, with the smallest Cr-Cr separation, has a CW temperature of $-390$ K and exhibits a transition from a paramagnet with strong quantum fluctuations into a complex planar antiferromagnet at $T_N = 12.5$ K, accompanied by a small tetragonal distortion [11,15]. The oxide is governed by direct AFM Cr-Cr exchange [16]. The ratio of CW to Néel temperature, defining the frustration parameter $f \equiv \Theta / T_N \sim 30$, signals strong geometrical frustration [17]. The structural phase transition has been explained in terms of a spin Jahn-Teller effect [11,12,18]. The selenide, ZnCr₂Se₄, with the largest Cr-Cr distance of the zinc-chromium spinels, has a positive CW temperature of 115 K and exhibits a transition into a helical magnetic structure at 20 K [13]. The helical structure is characterized by ferromagnetic (001) planes with a propagation vector along the [001] axis [19]. The increase of the lattice constant in the selenide almost suppresses the direct exchange and the spin arrangement follows from the dominating ferromagnetic 90° Cr-Se-Cr exchange and the additional influence of AFM interactions (some reminder of the direct exchange, plus nnn Cr-S-Zn-S-Cr and Cr-S-S-Cr exchange). Again, the magnetic phase transition is accompanied by a small tetragonal distortion with $1 - c/a = 0.001$ [20].

The sulfide, ZnCr₂S₄, lies exactly in between these two extremes. Consequently, FM and AFM exchange interactions almost compensate each other yielding a CW temperature of approximately 0 K. Neutron-scattering experiments [21] reveal a magnetic phase transition at 15.5 K into a helical spin order very similar to that in the selenide. Below 12 K a second commensurate collinear antiferromagnetic phase starts to gradually develop down to 8 K. This second phase has a similar spin arrangement like the AFM oxide. At low temperatures both magnetic phases coexist [21]. This fact already documents that both spin structures are characterized by almost the same free energy. The metastable magnetic ground state comes along with the competing FM and AFM exchange of almost equal strength, a situation we term as bond frustration. So far structural phase transitions in ZnCr₂S₄ have not been reported to occur along with the magnetic transitions. In reference [21] an upper limit of $1 - c/a < 0.002$ has been established. However, we would like to note that in all Zn-Cr spinels the structural phase transition yields marginal distortions only and can hardly be detected using standard diffraction techniques. Here we use infrared spectroscopy to probe...
structural transitions and spin-lattice correlations.

Polycrystalline ZnCr$_2$S$_4$ was prepared by solid-state reaction from high purity elements at 800°C. X-ray diffraction analysis at room temperature revealed single-phase material with the cubic spinel structure with a lattice constant $a = 9.983(2)$ Å and a sulfur fractional coordinate $x = 0.258(1)$. The magnetic properties were measured using a commercial SQUID magnetometer (Quantum Design MPMS-5). The heat capacity was monitored in a Quantum Design PPMS for temperatures $2 \text{ K} < T < 300 \text{ K}$ and in external magnetic fields up to 70 kOe. The thermal expansion was measured by capacitive method in fields up to 70 kOe. The reflectivity experiments on ceramic samples with polished surfaces were carried out in the far infrared (FIR) range using the Fourier-transform spectrometer Bruker IFS 113v in a He bath cryostat.

FIG. 1 presents the inverse susceptibility $\chi^{-1}$ vs temperature at different external magnetic fields. On approaching the Néel temperature $T_{N1}$ the specific heat exhibits a sharp $\lambda$-type anomaly. At lower temperature, a second anomaly at $T_{N2}$ becomes evident as a peak on heating and a kink on cooling. Note that this is the ordinary way in which the hysteresis at a first-order transition becomes evident in the relaxation method used [22]. The anomaly at $T_{N2}$ in the specific heat correlates with the respective anomaly observed in the susceptibility. Strong spin-lattice coupling and possible structural instabilities connected with both magnetic transitions can be deduced from the thermal expansion which exhibits significant anomalies both at $T_{N1}$ and $T_{N2}$ (Fig. 2). In zero magnetic field the thermal expansion coefficient $\alpha$ at the lower transition is by a factor of 4 larger and again reveals a significant hysteresis in accordance with the first-order character and, thus, the importance of the spin-lattice correlations. Magnetic field has a strong effect on the specific heat and thermal expansion, shifting the maximum in $C/T$ at $T_{N1}$ to lower temperatures as usually observed in antiferromagnets. A shift to lower $T$ is found also for the max-

FIG. 2: (color online) a) Heat capacity of ZnCr$_2$S$_4$ plotted as $C/T$ vs $T$ measured on cooling (closed symbols) and heating (open symbols) for 0 and 70 kOe. b) Temperature dependence of the thermal expansion coefficient at different external magnetic fields. Vertical lines indicate the phase transitions $T_{N1}$ and $T_{N2}$ in zero field.

at around $T_{N2} = 8$ K. In addition, we observed a pronounced difference between the susceptibilities measured on cooling and heating being maximal at $T_{N2}$. Such a hysteresis indicates a first-order transformation. Both magnetic anomalies are in good agreement with the early neutron-diffraction experiments [21]. In the following we demonstrate that the anomalies in the susceptibility correlate with respective anomalies found in the specific heat, thermal expansion and IR spectra.

The inset in Fig. 1 provides a closer look to the transition region. In a narrow temperature range around $T_{N1}$, our results are similar to those obtained on polycrystalline and single-crystalline samples in [21]. However, below $T_{N1}$ after a continuous drop the susceptibility exhibits a sharp change of slope
exchange and, hence, stabilizes the helical spin arrangement ordered state primarily depends on the type of coupling: ferromagnetic or antiferromagnetic, with the latter revealing positive shifts of the phonon eigenfrequencies in the magnetically induced FM component. This corroborates our interpretation that the helical spin structure in ZnCr$_2$S$_4$ is supported by FM exchange, as already documented in ZnCr$_2$Se$_4$, which has a large and positive CW temperature and reveals a helical spin structure as stable ground state. At the same time, the complex collinear structure below $T_{N2}$ is supported by AFM exchange, in close analogy to strongly geometrically frustrated ZnCr$_2$O$_4$. In ZnCr$_2$S$_4$, the external magnetic fields break the balance of FM and AFM exchange interactions in favor of FM exchange and, hence, stabilizes the helical spin arrangement as revealed by the specific-heat and thermal-expansion experiments. The existence of strong spin-phonon coupling, which follows from the thermal-expansion data, is microscopically probed by means of IR spectroscopy.

For spinel compounds which show strong spin-phonon coupling effects [23, 24, 25, 26] it is well established that the sign of shift of the phonon eigenfrequencies in the magnetically ordered state primarily depends on the type of coupling: ferromagnetic or antiferromagnetic, with the latter revealing positive shifts of the eigenfrequencies [25, 26]. The main magnetic coupling mechanism in sulfides is superexchange which includes nn FM Cr-S-Cr and nm AFM Cr-S-Zn-S-Cr or Cr-S-S-Cr exchange interactions [13, 14]. From a thorough eigenmode analysis [24] it is known that the low-lying modes involve vibration of the Zn-S units, while Cr-S atoms are mostly involved in the high-frequency modes. For the spinels with FM ground states like CdCr$_2$S$_4$ [25] as well as for ferrimagnetic FeCr$_2$S$_4$ [26], it has been demonstrated that the low-lying modes reveal large and positive shifts due to AFM exchange, while negative shifts have been observed for the high-frequency modes. But in all these cases no splitting of the phonon modes could be detected at $T_c$, which seems to be clear as the FM spin order does not involve any lattice-symmetry breaking. A significant phonon splitting has been reported at the AFM phase transition in ZnCr$_2$O$_4$ which is accompanied by a small tetragonal distortion [27]. Recently, this phonon splitting has been interpreted as driven only by spin correlations in the collinear AFM spin structure, where the magnetically induced symmetry breaking appears only in the dynamic phonon properties, but preserving the cubic structure [28]. The effect of phonon splitting due to magnetic ordering even in the absence of any structural symmetry breaking has been predicted earlier by Massidda et al. [29].

Our room-temperature IR results on ZnCr$_2$S$_4$ are in good agreement with previously published data [30]. The IR spectrum reveals the four group-theoretically allowed phonon modes. A fit using a sum of Lorentz oscillators yields eigenfrequencies at 115, 244, 336, and 388 cm$^{-1}$. On decreasing temperature we find a positive frequency shift of the phonon eigenmodes, but below the magnetic phase transition temperatures all phonon modes reveal a clear splitting indicating a symmetry breaking as illustrated in Fig. 3. The eigenfrequency for all phonon modes as function of temperature is presented in Fig. 4 on a semilogarithmic plot. From room temperature down to 20 K the purely anharmonic behavior of a cubic spinel naturally describes the results. Below the first magnetic transition into the helical structure all main modes reveal an additional shift towards higher frequencies, as expected for AFM transitions. The shift is of the order of 0.5% for the high and of the order of 1% for the low-frequency modes. As the most important result we find that the splitting of the phonon modes does not occur at the same temperature: The high-frequency modes reveal significant splitting certainly at $T_{N1} = 15$ K: A weak but clearly pronounced shoulder is visible already at 14 K. At 5 K the splitting of both high-frequency phonons amounts approximately 1%. Contrary, the two low-frequency modes split distinctly below $T_{N1}$. The modes at 125 and 255 cm$^{-1}$ reveal single-mode behavior still at 11 K, and split at $T = 7$ close to $T_{N2} = 8$ K. At 5 K the mode splitting results in extra peaks for both modes and in a significant shoulder for the phonon at 260 cm$^{-1}$, which indicates a splitting into three modes at low temperatures. The overall splitting is of the order of 5% for both low-frequency modes.

The splitting of the IR-active modes in ZnCr$_2$S$_4$ at the two magnetic phase transitions further supports our interpretation. As outlined above, the high-frequency modes involve vibrations mostly of Cr-S atoms. The FM 90° Cr-S-Cr exchange governs the helical order of ferromagnetic (001) planes. This exchange interaction is responsible for the splitting of the high-frequency modes. But ZnCr$_2$S$_4$ is equally dominated by AFM exchange which establishes the complex commensurate collinear spin order. These AFM exchange interactions involve mainly Zn-S bonds which on the other side are involved in eigenfrequencies of the low-lying modes: Consequently, at $T_{N2}$ these modes are expected to split as we experimen-

![FIG. 3: (color online) Reflectivity for three phonon modes of ZnCr$_2$S$_4$ at temperatures around the magnetic transitions.](image-url)
ometrically frustrated ZnCr spin-phonon coupling. This has been established for the geometry breaking in the Zn-Cr spinels mainly results from a strong bonds - the new modes which appear at $\omega_N$ represent the mode of the high-temperature phase; closed symmetries of the all phonon modes on a semilogarithmic plot. Open symmetries

FIG. 4: (color online) Temperature dependence of the eigenfrequencies of all phonon modes for a ZnCr$_2$S$_4$ single crystal.

beside the anomaly at the Néel point. Our results reveal strong spin-phonon coupling that generates the low-temperature instability in ZnCr$_2$S$_4$. Suppression of the splitting of low-frequency phonons and concomitantly of the anomalies in the specific heat and thermal expansion by strong magnetic fields suggests a spin-driven origin of this transformation.

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