Large Magnetostriction and Negative Thermal Expansion in the Frustrated Antiferromagnet $ZnCr_2Se_4$

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A detailed investigation of $ZnCr_2Se_4$ is presented which is dominated by strong ferromagnetic exchange but orders antiferromagnetically at $T_N = 21$ K. Specific heat and thermal expansion exhibit sharp first-order anomalies at the antiferromagnetic transition. T_N is shifted to lower temperatures by external magnetic fields and finally is fully suppressed by a field of 65 kOe. The relative length change $\Delta L/L(T)$ is unusually large and exhibits negative thermal expansion α below 75 K down to T_N indicating strong frustration of the lattice. Magnetostriction $\Delta L/L(H)$ reveals large values comparable to giant magnetostrictive materials. These results point to a spin-driven origin of the structural instability at T_N explained in terms of competing ferromagnetic and antiferromagnetic exchange interactions.

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Recently, magnetic spinels have attracted considerable attention. Within the past few years exotic phenomena and fascinating ground states have been observed in this class of materials: heavy-fermion behavior [1], complex spin order and spin dimerization [2–4], spin-orbital liquid [5], and orbital glass [6], as well as coexistence of ferromagnetism and ferroelectricity [7,8]. They are attributed to the cooperativity and competition between charge, spin, and orbital degrees of freedom, all of which are strongly coupled to the lattice. In addition, topological frustration due to the tetrahedral arrangement of the magnetic cations and bond frustration due to competing ferromagnetic (FM) and antiferromagnetic (AFM) exchange interactions hamper any simple spin configuration in the ground state. Spin-lattice coupling plays an important role in releasing frustration by structural transformation. For example, in AFM chromium-oxide spinels frustration of the spins due to geometrical constraints is released by a Peierls-like structural transition explained in terms of a so-called spin Jahn-Teller effect [9–11]. Another source of a structural instability was recently identified in AFM $ZnCr_2S_4$ and ascribed to competing FM and AFM exchange of nearly equal strength yielding strong bond frustration [12].

Here we present the results of a study of the spin-lattice correlations of another zinc chromium spinel, $ZnCr_2Se_4$, which shows an AFM ground state despite the presence of strong FM exchange. Previous neutron-diffraction investigations revealed a complex AFM order below 20 K contrasting with the dominating FM interactions evidenced by a large positive Curie-Weiss (CW) temperature of 115 K [13,14]. The spin structure is incommensurate helical having a FM arrangement in the (001) planes with a turning angle of 42° between the spins in adjacent (001) planes. The transition to the AFM state at T_N is accompanied by a structural transformation from cubic $Fd\bar{3}m$ to tetragonal $I4_1/amd$ symmetry with a small contraction along the c axis of $c/a = 0.9999$ [15]. Recent neutron-diffraction and x-ray studies using synchrotron radiation defined an orthorhombic $Fddd$ symmetry of the low temperature phase [16]. This structural transformation cannot originate from a conventional Jahn-Teller instability, because the half-filled t_{2g} ground state of the Cr^{3+} ions is orbitally nondegenerate. However, as is well documented in literature, many chromium spinels manifest structural instabilities accompanying the magnetic order. In $ZnCr_2O_4$ with strong geometrical frustration of spins coupled by direct AFM Cr-Cr exchange [17], the transition from a paramagnet with strong quantum fluctuations into a planar antiferromagnet at $T_N = 12.5$ K occurs along with a small tetragonal distortion [2,9,16]. In $ZnCr_2S_4$ the FM Cr-S-Cr and AFM exchange interactions almost compensate each other yielding a CW temperature close to zero. $ZnCr_2S_4$ shows two subsequent AFM transitions at 15 and 8 K [18], which are accompanied by pronounced thermal and phonon anomalies suggesting the structural transformation related to competition of FM and AFM exchange interactions [12]. In $ZnCr_2Se_4$ the direct exchange is almost suppressed and the spin arrangement follows from the dominating FM Cr-Se-Cr exchange and the additional AFM interactions [19]. We use susceptibility, electron-spin resonance (ESR), specific heat, and thermal expansion to probe the spin-lattice correlations and to elucidate the origin of the structural instability in $ZnCr_2Se_4$.

The single crystals were grown by liquid transport between 900 and 950 °C. X-ray diffraction revealed a single-phase material with the cubic spinel structure with a lattice constant $a = 10.498(2)$ Å and a selenium fractional coordinate $x = 0.260(1)$. The magnetic properties were studied using a commercial SQUID magnetometer (Quantum Design MPMS-5) up to 50 kOe and a dc extraction magnetometer (Oxford Instruments) up to 100 kOe. The heat capacity was measured in a Quantum Design physical properties measurement system for temperatures $2 < T < 300$ K and in fields up to 70 kOe. The thermal expansion

was measured by a capacitive method in fields up to 70 kOe. The ESR studies were carried out with a Bruker ELEXSYS E500 CW spectrometer at X-band frequency ($\nu = 9.36$ GHz) in a helium gas flow cryostat (Oxford Instruments) for $4.2 \leq T \leq 300$ K.

Figure 1(a) presents the susceptibility χ versus temperature. At 21 K, χ shows a pronounced maximum with a steep drop followed by a smooth continuous decrease towards lower T. The temperature of 21 K marks the onset of AFM order at T_N identified by neutron diffraction [14,16]. Above 200 K, χ follows a Curie-Weiss law with a positive CW temperature $\Theta = 90$ K [inset of Fig. 1(a)] and an effective moment of $4.04\mu_B$ close to the spin-only value of $3.86\mu_B$ for Cr^{3+} ions in a $3d^3$ configuration. Above T_N the system is cubic without any preferred crystallographic axes. Below T_N due to the structural transformation one has to expect a distribution of tetragonally distorted domains. Indeed, below T_N the magnetization M measured along the $\langle 001 \rangle$ axis shows a change of slope at a critical field H_{c1} of about 10 kOe for $T = 2$ K characteristic for a metamagnetic transition [Fig. 1(b)]. This feature corresponds to the reorientation of domains according to the nearly equivalent crystallographic principal axes. Along the $\langle 111 \rangle$ axis smaller hysteresis features are obtained below but identical results above H_{c1}, indicating that the spiral direction is determined by the direction of the external magnetic field. The second critical field H_{c2} (which for $T = 2$ K is 65 kOe) corresponds to the breakdown of the helical spin arrangement. Beyond H_{c2} the magnetization M reaches the full saturation of about $3\mu_B$ per Cr ion.

Figure 2(a) shows the specific heat in the representation C/T vs T at different magnetic fields. For $H = 0$, C/T manifests a sharp anomaly on approaching the Néel temperature T_N. The peak in C/T at T_N is much sharper than for conventional antiferromagnets and points towards a first-order transition. Application of magnetic fields suppresses the peak in C/T and concomitantly shifts it to lower temperatures. The anomaly is fully suppressed by a field of 65 kOe where the helical spin arrangement is completely destroyed. The entropy involved in the AFM transition, calculated by integrating $(C_0 - C_{70\ \mathrm{kOe}})/T$ over the transition region, of 2.1 $\mathrm{J\,mol^{-1}\,K^{-1}}$, is surprisingly low, reaching only 9% of the full entropy of $2R\ln 4$ expected for the complete alignment of the Cr spins. Assuming that the magnon contribution to the specific heat for 0 and 70 kOe does not differ too much, this anomalously low transition entropy reveals that the main part of the spin entropy is released already at $T \gg T_N$. This indicates strong spin fluctuations in the paramagnetic regime characteristic for highly frustrated magnets.

Figure 2(b) presents the relative length change of the sample $\Delta L(T)/L_0 = [L(T) - L_0]/L_0$ at different magnetic fields, where L_0 is the length of the sample in a monodomain state at 4.3 K and $H = 0$. $\Delta L/L_0$ exhibits a strong drop at T_N. Figure 2(c) illustrates the respective variations of the thermal expansion $\alpha = (1/L)dL/dT$

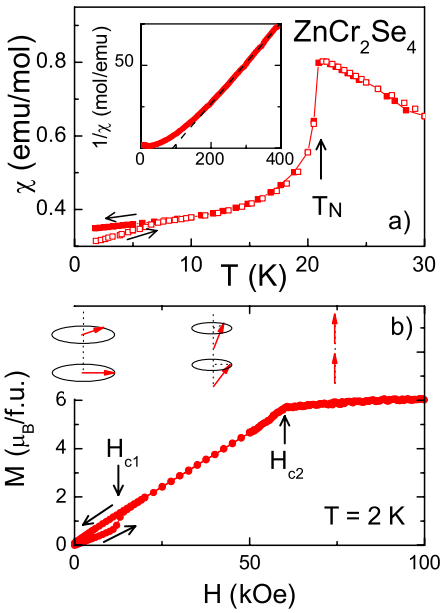

FIG. 1 (color online). (a) Susceptibility versus temperature at low temperatures for a $ZnCr_2Se_4$ single crystal. Inset: Inverse susceptibility versus T at 10 kOe. The dashed line indicates a Curie-Weiss behavior. (b) Magnetization curve for a field applied along the $\langle 001 \rangle$ direction at 2 K. Critical fields H_{c1} and H_{c2} are indicated. The evolution of the magnetic structure in an external field is shown.

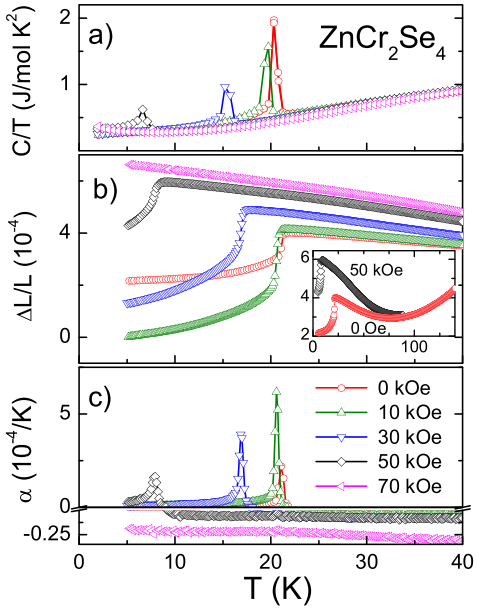

FIG. 2 (color online). (a) Temperature dependence of the heat capacity of a $ZnCr_2Se_4$ single crystal plotted as C/T vs T. (b) Relative length change of the sample $\Delta L(T)/L_0$. Data are normalized to the monodomain state at $H = 0$ and $T = 4.3$ K. Inset: $\Delta L(T)/L_0$ for an extended temperature range illustrating the negative thermal expansion between T_N and 75 K in $H = 0$ and 50 kOe. (c) Thermal expansion α at different magnetic fields between 0 and 70 kOe applied along the $\langle 001 \rangle$ axis.

being the slope of the relative length change. It manifests a steep narrow maximum at T_N for zero field, which shifts to lower T and broadens with increasing field similarly to the anomaly in the specific heat. In contrast to the specific heat, the amplitude of the maximum in α at the T_N shows a nonmonotonous variation with magnetic field which can be related to a polydomain state in $H = 0$. It increases with the field up to the critical value H_{c1} of the metamagnetic transition and then decreases for higher fields. Such a behavior for low fields can be attributed to the reorientation of magnetic domains with three different nearly equivalent $\langle 001 \rangle$ axes being the spiral propagation direction in agreement with the magnetization measurements [20]. Above H_{c1} a monodomain state with a spiral vector parallel to the external magnetic field is established which enhances the relative length change of the sample.

The most important feature of $\Delta L/L$ is a strong negative thermal expansion observed below 75 K down to T_N as reflected by negative slope shown in Fig. 2(b) and in the inset of this figure. It is interesting to note that in a field of 70 kOe a nearly constant negative thermal expansion evolves resulting in an approximately linear decrease of the sample length with increasing temperature up to 75 K. Negative thermal expansion could result from geometrical frustration of the lattice degrees of freedom [21] and is usually explained by highly anharmonic vibrational modes [22]. In $ZnCr_2Se_4$ it can be attributed to strong coupling of the phonons to the spin degrees of freedom. Indeed, recent infrared-spectroscopy studies of this compound have found a splitting of the low frequency phonon at T_N and a strong softening of the high frequency phonons below 100 K, which we associate with the negative thermal expansion [23].

The magnetostriction below and above T_N is illustrated in Fig. 3. The monotonous increase of $\Delta L(H)/L_0$ observed above T_N changes into an initial decrease up to the metamagnetic transition followed by a stronger increase up to the saturation field below T_N. Note the unusually high value of the magnetostriction, which is comparable to that observed in giant magnetostrictive materials with strong spin-orbital coupling [24] and geometrically frustrated $CdCr_2O_4$ spinel [25]. Note that no strong spin-orbital coupling is active here, as has been additionally proven by the electron-spin resonance. In $ZnCr_2Se_4$ the magnetostriction is driven by the shift of the phase transition in an external field in analogy to effects of colossal magnetoresistance [26] or colossal magnetocapacitance [7] observed in this class of spinel compounds.

The ESR absorption of the Cr spins in $ZnCr_2Se_4$ in the paramagnetic regime consists of a single exchange-narrowed Lorentz line. Figure 4 shows the T dependence of the resonance field H_{res} and linewidth ΔH for a disk with (110) plane orientation for $21 < T < 300$ K. From H_{res} we derived an asymptotic g value of 1.996 at high temperatures close to the spin-only value in agreement with the susceptibility results. This additionally indicates only minor spin-orbit coupling typical for Cr^{3+} ions [27].

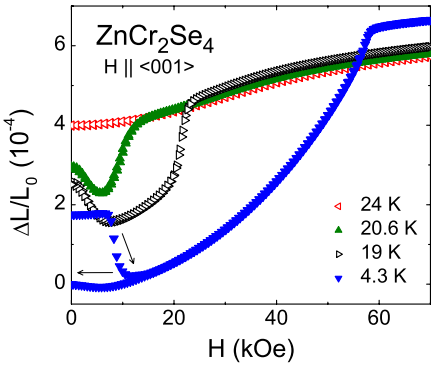

FIG. 3 (color online). Longitudinal magnetostriction $\Delta L(H)/L_0$ of a $ZnCr_2Se_4$ single crystal at several temperatures below and above T_N.

Approaching T_N, H_{res} strongly decreases as often observed close to the onset of AFM order due to the opening of the excitation gap. The T dependence of the intensity at resonance absorption compares well with the bulk susceptibility indicating the same Curie-Weiss law at high temperatures [inset of Fig. 4(a)]. The linewidth ΔH, which is a measure of the spin correlations, strongly increases when approaching T_N. For an exchange coupled spin system outside the critical regime and above the phase transition, the temperature dependence of the ΔH should be proportional to $\Delta H_\infty/(T\chi)$ where ΔH_∞ denotes the

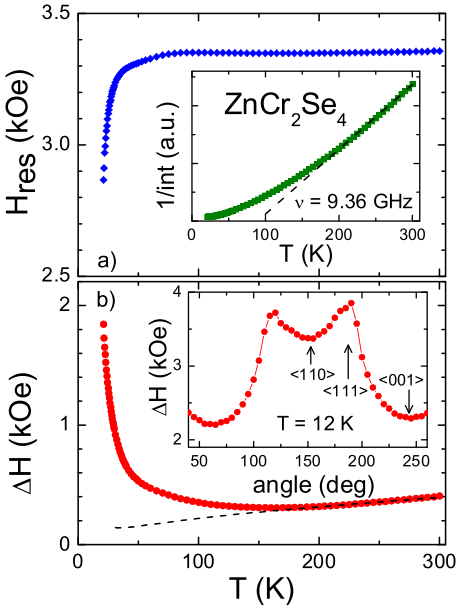

FIG. 4 (color online). Temperature dependence of the resonance field (a) and linewidth (b) for a single crystalline $ZnCr_2Se_4$ disk with (110) plane orientation. The dashed line indicates the expected behavior for an exchange coupled system. Upper inset: inverse intensity of the ESR line versus T, showing a Curie-Weiss dependence at high temperatures. Lower inset: angular dependence of the linewidth at 12 K, revealing significant magnetocrystalline anisotropy.

asymptotic high-temperature linewidth [28]. Deviations from this expected behavior, indicated by the dashed line in Fig. 4(b), set in already below 200 K signaling significant spin fluctuations due to strong exchange interactions despite the low ordering temperature. This highlights the competition of FM and AFM interactions evident from the corresponding high-temperature deviation of the susceptibility from the CW law. Below T_N a broad absorption band is observed centered on zero magnetic field. The angular dependence of the corresponding linewidth is shown in the inset of Fig. 4(b). It reflects a cubic anisotropy with a maximum at $\langle 111 \rangle$ and minima at $\langle 110 \rangle$ and $\langle 001 \rangle$ axes indicating strong coupling of the magnetization to the lattice in agreement with the earlier higher frequency ESR results [29].

The obtained data reveal a strong spin-lattice coupling and provide experimental evidence for a spin-driven origin of the structural transformation from the high-temperature cubic phase to a lower symmetry below the magnetic transition at T_N. The dominant magnetic coupling mechanism in $ZnCr_2Se_4$ is superexchange, which includes FM Cr-Se-Cr and AFM Cr-Se-Zn-Se-Cr or Cr-Se-Se-Cr exchange interactions [19]. These competing interactions establish the complex spin configuration. The FM 90° Cr-Se-Cr exchange governs the ferromagnetic order in the (001) planes. The AFM exchange is probably responsible for the spin arrangement between the adjacent (001) planes. An external magnetic field changes the balance between FM and AFM interactions enhancing the ferromagnetic correlations and reduces the angle between the spins in the adjacent FM planes. In agreement with our observation of the concomitant reduction of the anomalies of specific heat and thermal expansion by a magnetic field, this corroborates the interpretation of the low-temperature structural symmetry breaking in $ZnCr_2Se_4$ as due to bond frustration caused by competing exchange. This results in an extremely large influence of the magnetic field on the structural transition. The negative thermal expansion indicates strong frustration of the highly symmetric lattice in the paramagnetic regime. This frustrated lattice is highly receptive to weak perturbations which are primarily induced by magnetic order at T_N. The coupling between the magnetism and lattice may be realized via an exchange-striction mechanism similar to a spin-Peierls transition. However, compared to the 3D spin Jahn-Teller transition in chromium-oxide spinels [9–11] and to the 1D spin-Peierls transition in $CuGeO_3$ [30], we observed a much stronger effect of a magnetic field on the structural transition, which we attribute to the strong bond frustration. The negative thermal expansion and strong spin-lattice coupling observed in related $CdCr_2S_4$ spinel [7] can probably be related to similar mechanisms.

In conclusion, we investigated the bond frustrated AFM spinel $ZnCr_2Se_4$ and found pronounced anomalies in the specific heat and thermal expansion at the onset of the helical order. Our results reveal strong spin-phonon coupling that generates the low-temperature structural instability. The observed negative thermal expansion results from the high frustration of the lattice degrees of freedom. A large magnetostriction comparable to giant magnetostrictive materials is found despite the absence of strong spin-orbital coupling of the half-filled Cr^{3+} t_{2g} electronic state. An extremely strong suppression of the anomalies in the specific heat and thermal expansion by external magnetic fields suggests a spin-driven origin of the structural transformation.

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