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Novel phase transition and metastable regions in the frustrated magnet $CdCr_2O_4$

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A new magnetic phase transition, which we assign to the separation of two different spiral phases, has been observed by ultrasound studies below the Néel temperature ($T_N = 7.8$ K) in the frustrated antiferromagnet $CdCr_2O_4$. This transition renormalizes the velocity and amplitude of the transverse acoustic mode c_T whereas the longitudinal mode c_L is not affected. The specific heat does not show any significant change in the entropy at this transition. Furthermore, in an applied magnetic field, the mode c_T exhibits extended metastable magnetostructural states neighboring the one-half magnetization plateau in $CdCr_2O_4$. By applying an exchange-striction model we can quantitatively describe the field dependence of the sound velocity below and above the one-half magnetization plateau.

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Frustrated magnetic systems with competing interactions are of great interest in solid-state physics. Frustration manifests in a number of fascinating properties, often with novel magnetic phases distinct from those of ordinary magnets or spin glasses [1]. Typical examples of frustrated magnetic systems are those with a magnetic pyrochlore lattice [2] which consists of corner-sharing tetrahedra, such as in the spinel $CdCr_2O_4$ with Cr^{3+} ions ($S = 3/2$) placed at each tetrahedron vertex. Despite strong magnetic exchange evidenced by the Curie-Weiss temperature $\Theta_{CW} \approx -70$ K, the antiferromagnetic (AFM) ordering in this material sets in just below $T_N = 7.8$ K, concomitant with a structural transformation from cubic ($Fd\bar{3}m$) to tetragonal ($I4_1/amd$) [3] due to a spin Jahn-Teller effect [4]. Neutron-scattering studies [5,6] show a long-pitched incommensurate coplanar-spiral spin configuration below T_N [ordering wave vector $\mathbf{Q} = 2\pi(0,\delta,1)$, $\delta = 0.09$] caused by weak Dzyaloshinskii-Moriya (DM) interactions [7].

$CdCr_2O_4$ is well known for its rich magnetic-field temperature phase diagram. A famous one-half magnetization plateau emerges between 28 and 58 T [8–10] with a configuration of three spins up and one spin down for each Cr^{3+} tetrahedron and a cubic $P4_332$ symmetry [3]. A transverse spin order above the plateau has been proposed [11] and a magnetic superfluid state below the saturation field has been recently suggested from magnetization and magneto-optical spectroscopy data [10]. The magnetic structures in this material as well as the role of lattice degrees of freedom have been analyzed in a number of works [12,13], however, the nature of the high-field phases is still not identified.

In this Rapid Communication, we report ultrasound experiments in pulsed fields up to 87 T, providing further insight into the intriguing physics of the high-field phases in $CdCr_2O_4$. We have observed a large, field-induced metastable magnetostructural region along with a new phase transformation presumably between two different magnetic spiral structures within the AFM state.

A high-quality single crystal of $CdCr_2O_4$ was grown from Bi_2O_3-V_2O_5 flux. The shape of the single crystal allowed us to perform ultrasound measurements along the [111] direction. Two opposite (111)-crystal surfaces were polished for the ultrasound experiments. The sample thickness along the [111] direction is 1.64 mm. $LiNbO_3$ resonance transducers with a fundamental frequency of 30 MHz were implemented to generate and detect transverse acoustic waves whereas wide-band polyvinylidene fluoride (PVDF) films were used to generate longitudinal acoustic waves. Typical ultrasound frequencies used in this study were fixed between 28 and 107 MHz. Temperatures down to 1.5 K were reached by use of ^{4}He cryostats placed inside a 20 T superconducting magnet and, for higher magnetic fields, a 90 T pulsed magnet [14,15]. A RuO_2 thermometer was thermally coupled to the sample. The magnetic field was applied along the sound-propagation direction. Here, the longitudinal $c_L = (c_{11} + 2c_{12} + 4c_{44})/3$ ($\mathbf{k}\|\mathbf{u}\|[111]$) and transverse $c_T = (c_{11} + c_{44} - c_{12})/3$ ($\mathbf{k}\|[111], \mathbf{u}\perp\mathbf{k}$) acoustic modes are studied, where $\mathbf{k}$ and $\mathbf{u}$ are the wave vector and polarization of the acoustic wave, respectively, and c_{ij} are the elastic moduli. The sound velocity $v(\mathbf{k},\mathbf{u})$ is related to the elastic modulus via $c_{ij} = \rho[v(\mathbf{k},\mathbf{u})]^2$, where ρ is the mass density of the crystal. More details are given in Refs. [16,17]. The specific heat was measured by use of the relaxation method [18] on a small piece cut from the ultrasound sample.

Figures 1(a) and 1(b) show the temperature dependence of the relative changes of the sound velocity $\Delta v/v$ and the sound attenuation $\Delta\alpha$ for the transverse acoustic mode c_T measured at various magnetic fields. Several prominent features appear in $\Delta v/v$ and $\Delta\alpha$ below 8.5 K. There is a large increase of 10% in the sound velocity near T_N, accompanied by an anomaly in the sound attenuation. As previously mentioned, the magnetic ordering in this material is a direct result of a first-order spin Jahn-Teller phase transition with a change of the crystallographic symmetry. As expected for a first-order phase transition, both acoustic properties exhibit pronounced hystereses. The phase transition shifts to lower temperatures

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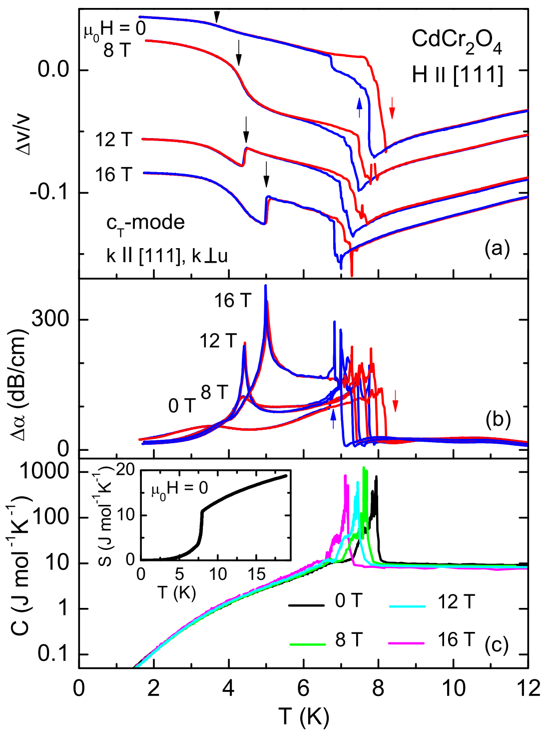

FIG. 1. (Color online) Temperature dependence of (a) the sound velocity $\Delta v/v$ and (b) the sound attenuation $\Delta\alpha$ of the transverse ultrasonic wave propagating along the [111] ($k\|H\|[111]$ and $u\perp k$) direction (acoustic c_T mode) at different magnetic fields. Results for up (red curves) and down (blue) temperature sweeps are shown. In (a) the data for different fields are shifted arbitrarily along the y axis for clarity. The black arrows indicate the position of the newly observed phase transition. The ultrasound frequency was 28.9 MHz. The temperature dependence of the specific heat at different magnetic fields is shown in (c). Results were obtained by use of the relaxation method during cooling. The inset shows the temperature dependence of the entropy calculated from the zero-field specific-heat data.

with increasing magnetic fields. Remarkably, in the ordered state, additional anomalies appear: deviations in the sound velocity and a maximum in the attenuation signal a new phase transition. These anomalies become more pronounced with increasing magnetic field with steps in the sound velocity and sharp λ-like peaks in the attenuation at higher fields, $B \geqslant 12$ T. The lack of a hysteresis suggests a second-order phase transition.

The specific heat, measured at the same magnetic fields [Fig. 1(c)], shows huge anomalies at T_N (please note the logarithmic scale of the ordinate), in agreement with previously reported data [19,20]. Due to the first-order character of the phase transition, multiple peaks appear just below T_N. These peaks are visible in the region only where the hystereses in the sound velocity and sound attenuation are found. At the same time, no specific-heat anomaly was detected at lower temperatures where the ultrasound data evidence the additional phase transition. Obviously, no detectable entropy change is accompanying this transition (inset of Fig. 1). The expected high-temperature entropy value for a spin system with $S = 3/2$ is $2R\ln(2S+1) \approx 23\ \mathrm{J\,mol^{-1}\,K^{-1}}$ [19,20]. The spin Jahn-Teller phase transition results in an entropy reduction

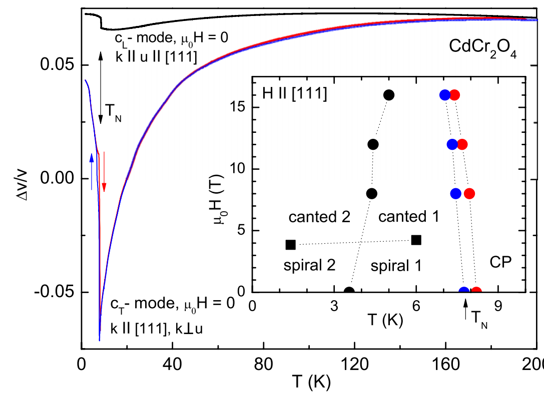

FIG. 2. (Color online) Temperature dependence of the sound velocity of the modes c_T and c_L in $CdCr_2O_4$. The data are shifted along the y axis for clarity. The upper curve is taken from Ref. [13] (Fig. 1). The inset shows the low-field part of the H-T phase diagram with the transitions extracted from the ultrasound data shown in Fig. 1. The squares mark the position of a phase transition observed in earlier work [13] (see also Fig. 3). The blue and red symbols represent the hysteretic region of the first-order transition. CP means cooperative paramagnetic state. See text for details.

of about 40% (inset of Fig. 1) while the phonon contribution is negligible in the shown temperature range.

Figure 2 shows the temperature dependence of the sound velocity of the modes c_T and c_L measured at zero field. We notice a much stronger renormalization of the sound velocity in approaching T_N for the transverse mode, c_T, than for the longitudinal one, c_L, signaling that the leading contribution to the exchange-striction coupling is proportional to the scalar product of the exchange gradient and the transversal polarization of the c_T mode. Moreover, the softening of the c_T mode due to the spin-phonon coupling starts at about 200 K, evidencing strong spin correlations in the cooperative paramagnetic (CP) state [13]. Remarkably, the onset of this softening happens at an unexpectedly high temperature ($T \approx 3|\Theta_{CW}|$).

The inset of Fig. 2 shows the H-T phase diagram as extracted from the ultrasound data. Note that the low-field part of the phase diagram below a field-induced phase transition observed in the sound velocity (Fig. 3, $\mu_0 H_c \approx 4$ T at 1.4 K) contains a metastable area characterized by a hysteretic behavior in the mode c_T. This transition as well as a similar anomaly observed at 6 K are marked by the squares in the H-T phase diagram in Fig. 2. The magnetization demonstrates a hysteresis in this region as well (Fig. 7 in Ref. [13]). Previously, the low-field phase has been ascribed to a long-ranged spiral state arising due to the DM interaction [7] with a first-order phase transformation to the four-sublattice canted state at about 5 T observed in electron spin resonance (ESR) [21] as well as in magnetization and ultrasound [13] measurements.

Sound-velocity measurements performed in pulsed magnetic fields up to 87 T have revealed further striking anomalies (Fig. 4). The most prominent features are huge metastable regions below and above the one-half magnetization plateau. These metastable regions are detected only in the transverse mode, whereas the longitudinal mode exhibits only minor hystereses within and just below the magnetization-plateau range (see also Fig. 8 in Ref. [13]). The hysteresis in

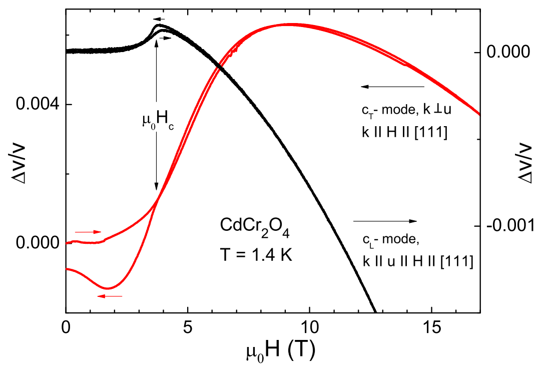

FIG. 3. (Color online) Field dependence of the sound velocity of the modes c_T (red) and c_L (black) at 1.4 K. The field-sweep directions are shown. The position of the field-induced phase transition is marked by $\mu_0 H_c$. Ultrasound frequencies were 29 and 107 MHz for the mode c_T and c_L, respectively. Note that the relative-velocity scale is different for the modes c_T (left side) and c_L (right side).

c_T vanishes at 83 T, where a spin-nematic state has been recently proposed [10]. Additionally, some fine features can be resolved in the ultrasound velocity of c_T at highest fields, namely, a sharp minimum followed by a step and a further smooth increase towards the saturated state. Magnetization in $CdCr_2O_4$ is fully saturated at about 88 T [10].

We discuss first the observed low-temperature phase transition. According to neutron-scattering measurements [6], six domains related to the elliptical spiral phases have to be considered in the tetragonal phase below $T_N \approx 8$ K. Consequently, the observed features in the sound velocity and attenuation around 3–5 K (Fig. 1) can be associated with a transition between two different domain configurations, one of which becomes energetically favorable at low temperatures. Such a transition could, for example, occur between the two degenerate spin-spiral domain states with $(0,\delta,1)$ and $(\delta,0,1)$. Here, $\delta \approx 0.09$ defines the pitch of the spirals [6].

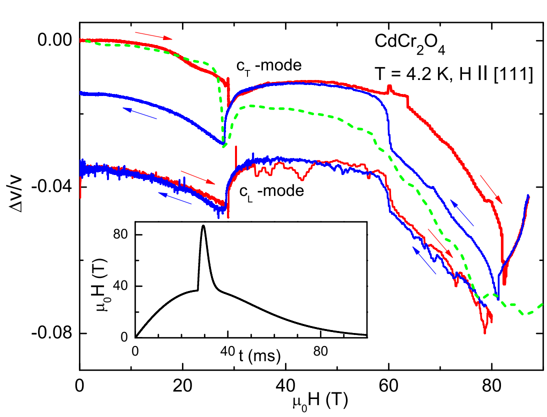

FIG. 4. (Color online) Field dependence of the sound velocity of the modes c_T and c_L at 4.2 K. Arrows indicate the field-sweep directions. The green dashed line presents calculated results (see text for details). The ultrasound frequencies were 106.5 and 60.5 MHz for mode c_T and c_L, respectively. The data for c_T and c_L are shifted arbitrarily along the y axis for clarity. The inset shows the time dependence of the magnetic-field pulses used in these experiments. The magnetic field is applied along the [111] direction.

The external magnetic field favors domains with spins oriented perpendicular to the magnetic field, explaining the occurrence of the strong anomalies at higher fields. It turns out that the striction caused by the sound wave itself can be the reason for the favored domain configuration at $H = 0$.

On the other hand, the observed low-temperature transition might be also related to the onset of an additional magnetic orthorhombic anisotropy (i.e., a and b being inequivalent), which would produce preferential directions for the distribution of magnetic moments in noncollinear magnetic structures. For both cases there would be no significant change in the entropy, in line with the absence of an anomaly in the specific heat. Further, stronger features are expected to appear for the transverse compared to longitudinal acoustic mode. This explains why the transverse mode c_T is more strongly influenced by the magnetic subsystem than the longitudinal mode c_L. A more detailed analysis is challenging due to the presence of six domains in the ordered state and needs additional study.

Now, we consider the influence of field-induced magnetic phase changes on the elastic properties (Fig. 4). We assume that the main contribution to the renormalization of the sound velocity is determined by the exchange-striction mechanism using the approach elaborated in Refs. [22,23]. By neglecting inhomogeneous contributions from the magnetic susceptibility and the magnetic anisotropy of the exchange integrals, the expression for the renormalization of the sound velocity due to the spin-phonon interaction can be approximated as (we use the notations in which $g\mu_B = k_B = \hbar = 1$)

$$\Delta v/v = -|G_0|^2(2\langle S^0\rangle^2 + T\chi_0)\left(\chi_0 + \frac{H_0}{2|G_0|^2}\right). \qquad (1)$$

Here, v is the sound velocity in the absence of spin-phonon interactions, $\langle S_0\rangle$ is the average spin moment (related to the magnetization) along the direction of the magnetic field H, and χ_0 is the uniform magnetic susceptibility. The renormalization is proportional to the exchange-striction coupling constants

$$G_0 = \frac{1}{Nm\omega_{\mathbf{k}}}\sum_n (e^{i\mathbf{k}\mathbf{R}_{nm}} - 1)\mathbf{u}_{\mathbf{k}}\frac{\partial J_{mn}}{\partial \mathbf{R}_m},$$
$$H_0 = \frac{4}{mN^2\omega_{\mathbf{k}}^2}\sum_n \cos^2(\mathbf{k}\mathbf{R}_{nm}/2)(e^{-i\mathbf{k}\mathbf{R}_{nm}} - 1) \times \mathbf{u}_{\mathbf{k}}\mathbf{u}_{-\mathbf{k}}\frac{\partial^2 J_{mn}}{\partial \mathbf{R}_n \partial \mathbf{R}_m}. \qquad (2)$$

Here, m is the mass of the magnetic ion, N is the number of spins in the system, $\omega_{\mathbf{k}} = vk$ is the low-k dispersion relation for the phonon, J_{mn} denote effective exchange integrals, $\mathbf{u}_{\mathbf{k}}$ is the polarization of the phonon with wave vector $\mathbf{k}$, $\mathbf{R}_n$ is the position vector of the nth site, and $\mathbf{R}_{nm} = \mathbf{R}_n - \mathbf{R}_m$. It is clear that the renormalization of the sound velocity in an external field is related to the magnetic-field dependence of the magnetization and magnetic susceptibility. We have used the high-field magnetization data at 4.2 K from Ref. [10] to calculate $\Delta v/v$. The resulting field-dependent sound velocity is shown in Fig. 4 as the dashed (green) line (with $G_0 \approx 0.2$ and $H_0/|G_0|^2 = 0.4$). The good agreement between experiment and theory up to ∼80 T allows one to conclude that the renormalization of the sound velocity in $CdCr_2O_4$ is mainly related to the exchange-striction mechanism. At higher fields one probably has to take into account inhomogeneities of the magnetic susceptibility to obtain better agreement between the exchange-striction theory and experiment.

The observed metastable magnetostructural states in $CdCr_2O_4$ might have a similar origin as in $CoCr_2O_4$, another spinel compound [24], where the transverse helical component of the magnetization is disordered at high magnetic fields, leading to the high-symmetry phase remaining metastable down to zero magnetic field. Remarkably, in both compounds the metastability persists only in the region where the longitudinal magnetization changes, whereas the one-half magnetization plateau in $CdCr_2O_4$ exhibits a rather stable structural configuration with cubic $P4_332$ symmetry [3]. The huge metastable magnetostructural states seem to be a characteristic feature of magnetically frustrated spinels.

Taking into account existing experimental data, it is plausible to assume the following sequence of low-temperature field-induced magnetic phases in $CdCr_2O_4$. An incommensurate, spiral structure transforms at about 5 T into a four-sublattice canted structure [21], followed by the one-half magnetization plateau between 28 and 58 T with three spins up and one spin down for each tetrahedron [8]. Another canted state is realized above the one-half magnetization plateau and persists almost to the saturation field [9]. Our results suggest that the metastable magnetostructural states exist together with the spiral and canted magnetic structures, below and above the plateau. Our sound-velocity measurements indicate another phase above 83 T which seems to exist up to the saturation field of 88 T. Note that from magnetization and magneto-optical absorption spectra [10] a magnetic superfluid state has been suggested to exist between 74 and 88 T, however, the nature of this high-field state is not clear yet and additional studies are needed.

In conclusion, we have studied the magnetic phase diagram and the role of magnetoacoustic interactions in the frustrated antiferromagnet $CdCr_2O_4$ by means of ultrasound measurements. A previously unknown transformation of the magnetic structure below T_N has been found. We ascribe this to a transition between different spiral (canted) phases. Metastable magnetostructural regions have been observed below and above the one-half magnetization plateau. The correlation between the anomalies in the magnetization and in the sound velocity demonstrates that the exchange-striction interactions play an important role in this material. We have shown that the transverse strain related to the acoustic c_T mode is particularly sensitive to these effects in $CdCr_2O_4$.

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