Spin-lattice coupling in the frustrated antiferromagnet $ZnCr_2Se_4$ probed by ultrasound

V. Felea,[1] S. Yasin,[2] A. Günther,[3] J. Deisenhofer,[3] H.-A. Krug von Nidda,[3] S. Zherlitsyn,[2] V. Tsurkan,[1,3] P. Lemmens,[4] J. Wosnitza,[2] and A. Loidl[3]

[1]*Institute of Applied Physics, Academy of Sciences of Moldova, MD 2028 Chisinau, Republic of Moldova*
[2]*Hochfeld-Magnetlabor Dresden (HLD), Helmholtz-Zentrum Dresden-Rossendorf, D-01314 Dresden, Germany*
[3]*Experimental Physics 5, Center for Electronic Correlations and Magnetism, Institute of Physics, University of Augsburg, D-86159 Augsburg, Germany*
[4]*Institute for Condensed Matter Physics, TU Braunschweig, D-38106 Braunschweig, Germany*

(Received 25 June 2012; published 14 September 2012)

Ultrasound and magnetization studies of the frustrated spinel $ZnCr_2Se_4$ are performed as a function of temperature and magnetic field up to 14 T. In zero field, the sound velocity and attenuation reveal significant anomalies at the antiferromagnetic transition at $T_N \approx 21$ K indicating strong spin-lattice coupling. External magnetic fields shift these anomalies to lower temperatures concomitantly with the reduction of the Néel temperature. At 2 K, the sound velocity as a function of magnetic field manifests three pronounced anomalies: a deep minimum at 5.4 T related to an inflection point of the magnetization followed by two plateaus with distinct stiffness at fields above 7 and 10 T. The first plateau is ascribed to a transformation from a tetragonal to a cubic phase, while the second one corresponds to a state with fully polarized magnetization. The evolution of magnetic and structural states is discussed within a H-T phase diagram and compared with related frustrated magnetic spinels with strong spin-lattice coupling.

DOI: 10.1103/PhysRevB.86.104420 PACS number(s): 43.35.+d, 62.65.+k, 72.55.+s, 75.50.Ee

I. INTRODUCTION

Magnetic materials with spinel structure are of continuous experimental and theoretical interest. They offer exceptional possibilities to study the interplay of spin, charge, and orbital degrees of freedom of magnetic ions on the background of a topologically frustrated lattice. Among the numerous exotic phenomena discovered in magnetic spinels,[1–15] recently magnetoelectric effects attracted particular attention.[16–20] The coexistence of long-range magnetic order and spontaneous dielectric polarization in the same material is quite promising for the design of novel magnetoelectronic devices with mutual electric and magnetic control.[21,22]

In fact, many spinels exhibiting multiferroic behavior also show strong spin-lattice coupling manifesting itself in negative thermal expansion, colossal magnetostriction,[12,13] and spin Jahn-Teller effects.[9–12,23–25] As a consequence of the magnetoelastic coupling structural transition can be induced by external magnetic fields.[15] The spinel compound $ZnCr_2Se_4$ was shown to undergo a helical antiferromagnetic (AFM) order below $T_N = 20$ K.[26,27] The AFM ordering contrasts with the dominating ferromagnetic (FM) spin correlations evidenced by a large positive Curie-Weiss (CW) temperature of 115 K. This suggests a strong bond-frustration effect related to competing FM and AFM exchange interactions. The spin structure is incommensurate having a FM arrangement in the (001) planes with a screw angle of 42° between the spins in adjacent (001) planes forming a helical configuration. The transition to the AFM state 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 with $c/a = 0.9999$.[28] Later neutron and x-ray synchrotron studies reported an orthorhombic $Fddd$ symmetry of the low-temperature phase.[29] Recent neutron-diffraction studies[30] revealed broad diffuse scattering in the temperature range where the negative thermal expansion is observed, namely from 80 K down to T_N.[12] These diffuse peaks were assigned to magnetic fluctuations and coexist with the main Bragg reflections even in the long-range-ordered phase.

In this study we report on ultrasound and magnetization studies of multiferroic $ZnCr_2Se_4$ performed in static magnetic fields up to 14 T to gain further insight into the magnetoelastic coupling. The sound velocity and the damping exhibit significant anomalies at the magnetic ordering transition and a softening of acoustic lattice modes on approaching the Néel temperature from above. Applying external magnetic field also results in a mode softening before the spiral spin structure is suppressed at a critical field H_{c2}. For fields larger than H_{c2} a field induced alignment of the spins sets in and the sound velocity indicates a conventional hardening of acoustic modes.

II. EXPERIMENT

$ZnCr_2Se_4$ single crystals were grown by chemical transport reactions using preliminary synthesized polycrystalline ternary compound. As the source of the transport agent (bromine) we used $TeBr_4$. This allows us to exclude contamination by halogen ions usually present in crystals prepared by chlorine transport. The growing process was performed between 850 and 900 °C during 3–4 weeks. X-ray powder-diffraction analysis of crashed single crystals confirmed the single phase spinel and the absence of foreign phases. The stoichiometry of the crystals was checked by the wavelength dispersive electron-probe microanalysis. The magnetic properties were studied using a commercial superconducting quantum interference device magnetometer (Quantum Design MPMS-5) up to 5 T and a dc extraction magnetometer (Oxford Instruments) up to 14 T. The measurements of the velocity and attenuation of longitudinal waves were performed with wave vector **k** and polarization **u** parallel to all three main crystallographic axes. In the following we only present the experimental data obtained for the ⟨001⟩ axis corresponding to the c_{11} acoustic mode for a cubic crystal, because the observed anomalies in sound velocity and magnetization appear at the same magnetic fields for all three main crystallographic axes without any sign of anisotropy. Ultrasonic studies were performed for temperatures between 1.5 and 150 K and in static magnetic fields up to 14 T utilizing an experimental setup with a phase-sensitive detection technique based on a pulse-echo method.[31]

III. RESULTS AND DISCUSSION

The magnetic susceptibility (Fig. 1) reveals a sharp peak at $T_N \approx 21$ K in a magnetic field of 0.01 T reflecting the transition into an AFM state. In higher magnetic fields applied along the ⟨001⟩ direction the susceptibility peak broadens and shifts to lower temperatures signaling the reduction of the Néel temperature in good agreement with specific-heat data which show a corresponding shift of the λ anomaly at T_N.[12]

Figures 2(a) and 2(b) show, respectively, the relative changes of the sound velocity, $\Delta v/v_0$, and of the attenuation α, measured in different static magnetic fields as function of temperature. In zero field, the sound velocity exhibits continuous stiffening on decreasing temperatures from 120 to 40 K (not shown) which can be attributed to usual anharmonic behavior. With further lowering temperatures, a significant softening is observed with an anomaly, i.e., a sharp minimum, in the sound velocity at T_N. The sound attenuation increases smoothly on approaching the magnetically ordered state and exhibits a sharp maximum at T_N. Both the sound velocity and attenuation show no hysteresis at T_N (when measured on cooling and warming) indicating closeness to a second-order phase transformation. With increasing magnetic field up to 3 T the magnitude of the anomalies in the sound velocity and attenuation at T_N grow enormously and shift to lower temperatures. In fields above 6 T, the sharp anomalies in the sound velocity and attenuation vanish, facts which correlate with the suppression of the antiferromagnetic helical order. The observed softening of the sound velocity in zero field on approaching T_N can be associated with the negative thermal expansion evidenced in earlier studies[12] and attributed to strong spin fluctuations in the paramagnetic state.

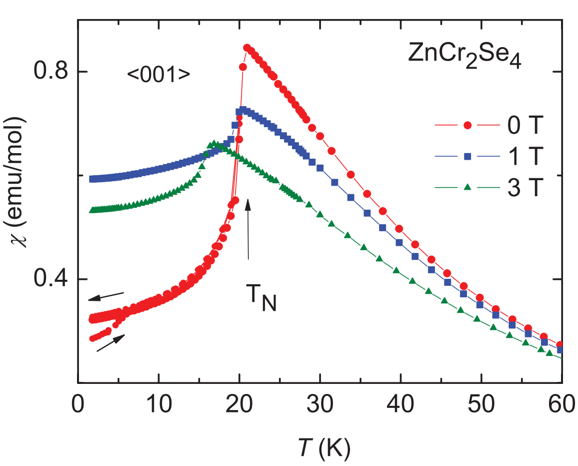

FIG. 1. (Color online) Temperature dependencies of the magnetic susceptibility for $ZnCr_2Se_4$ measured in different static magnetic fields applied along the ⟨001⟩ axis. The vertical arrow marks the magnetic phase transition at T_N in a field of 0.01 T.

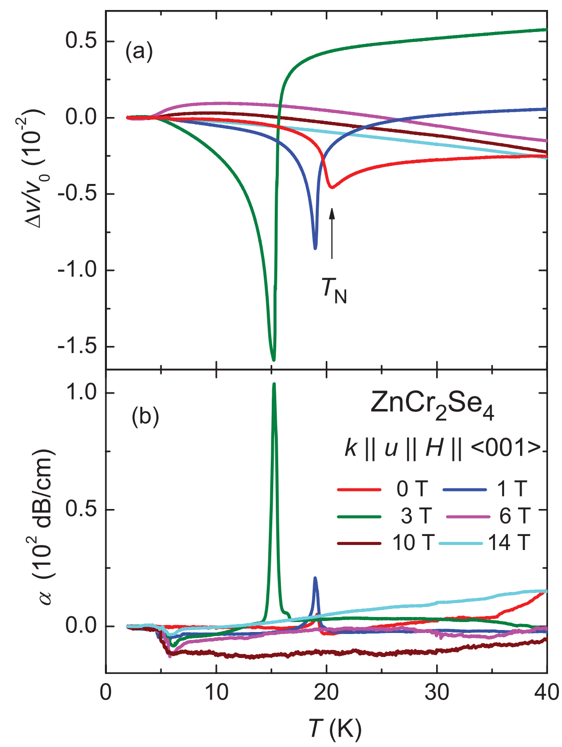

FIG. 2. (Color online) Temperature dependencies (a) of the relative change of the sound velocity, $\Delta v/v_0$, and (b) of the sound attenuation α, for $ZnCr_2Se_4$ measured in different magnetic fields applied along the ⟨001⟩ axis. v_0 is the sound velocity at 2 K at a given magnetic field. The vertical arrow marks the magnetic phase transition at T_N in zero field. The ultrasound frequency was set to 62 MHz.

In Figs. 3(a) and 3(b) the relative change of the sound velocity and of the attenuation as a function of magnetic field are shown for different temperatures. At 2 K, the sound velocity (attenuation) shows a deep minimum (sharp maximum) at 5.4 T with a sound-velocity change of 3.3%. With further increasing field, the sound velocity exhibits a sharp increase and then tends to saturate. Besides the sharp anomaly, the sound velocity exhibits two plateaus at fields above $H_{c2} \sim 6.5$ T and $H_{c3} \sim 10$ T, respectively indicating transitions to magnetostructural states with distinct stiffness. At 2 K and 10 T a well defined steplike increase of the sound velocity is clearly documented in Fig. 3(a) (H_{c3}). A concomitant anomaly was also observed in the field dependence of the damping [see inset of Fig. 3(b)]. The second plateau in fields above 10 T is also clearly discernible in the field dependence of the sound velocity at 8 K. Additional measurements in pulsed magnetic fields up to 62 T did not reveal any further changes in the sound velocity above 14 T (data not shown). With increasing temperatures, the sharp anomalies in the sound velocity and attenuation are shifted to lower fields. They fully disappear for temperatures above T_N where $\Delta v/v_0$ and α vary only slightly with field.

To understand the origin of the observed anomalies in the sound velocity and attenuation we measured the field

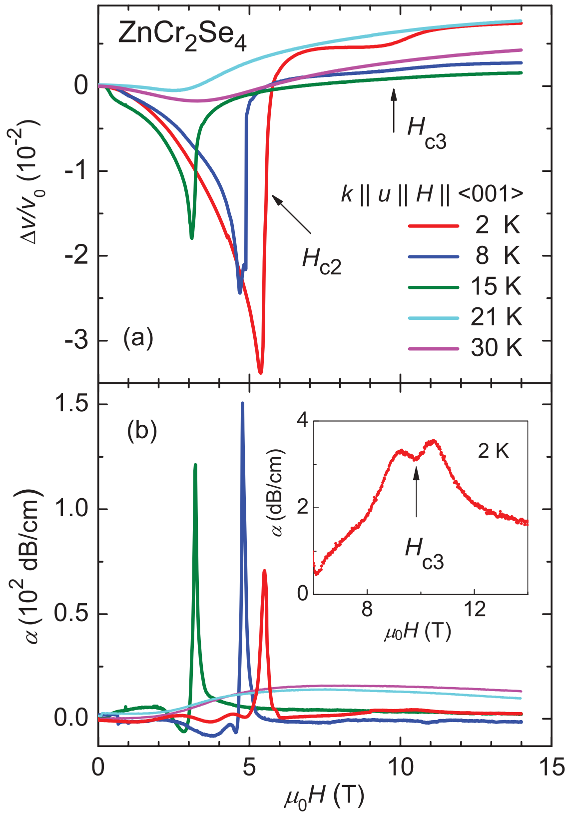

FIG. 3. (Color online) Relative change of the (a) sound velocity $\Delta v/v_0$ and (b) attenuation α vs magnetic field at different temperatures in $ZnCr_2Se_4$. v_0 is the sound velocity at 0 T at a given temperature. The vertical arrows mark the fields H_{c2} and H_{c3} of transitions to plateau states. The ultrasound frequency was set to 48.4 MHz. The inset shows the anomaly of attenuation α at H_{c3} on an enlarged scale.

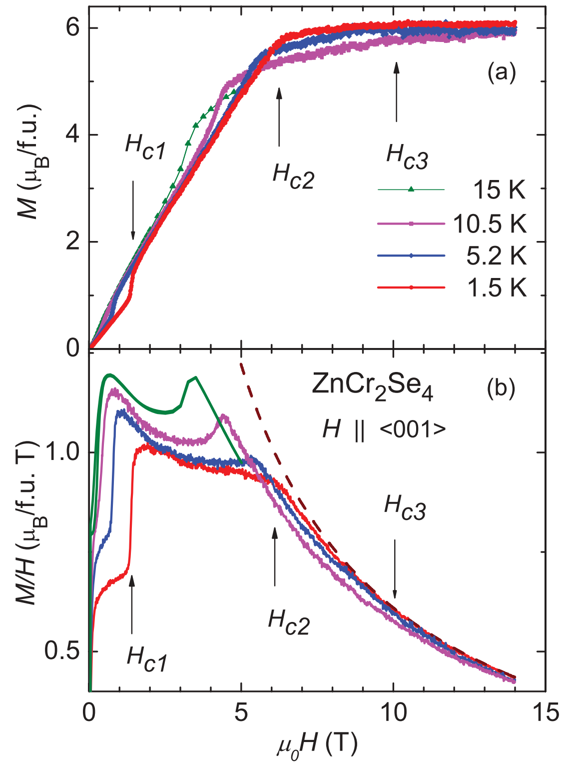

FIG. 4. (Color online) (a) Magnetization curves at different temperatures for $ZnCr_2Se_4$ measured along the $\langle 001 \rangle$ axis. (b) Susceptibility M/H for the same set of data. Arrows indicate the critical fields H_{c1}, H_{c2}, and H_{c3} for 1.5 K. The dotted line presents the saturation dependence $\chi = M_s/H$, where M_s is the saturation magnetization.

dependencies of the magnetization at different temperatures. The results are presented in Figs. 4(a) and 4(b) which show, respectively, the magnetization M and the susceptibility $\chi = M/H$ as a function of magnetic field. At 1.5 K, the magnetization shows an anomaly at $H_{c1} = 1.5$ T related to the reorientation of magnetic domains followed by a linear increase with increasing field up to $\sim$5.5 T. This domain reorientation at external magnetic fields H_{c1} is also visible in the temperature dependence of the susceptibility as measured at 0.01 T (see Fig. 1). For fields above H_{c1} the spiral planes are aligned perpendicular to the external field with the normal vector of the planes in field direction. For further increasing fields the spin spiral transforms into a cone with ferromagnetic moment. However, even at 2 K the full ordered moment is not reached at H_{c2}. But with further increasing fields the magnetization still grows reaching full saturation for fields larger than $H_{c3} \simeq 10$ T. The ordered moment of $6\mu_B$/f.u. corresponds to the ferromagnetic alignment of the spins of the Cr^{3+} ions in the $3d^3$ configuration with $S = 3/2$.

The change in the magnetization between H_{c2} and H_{c3} becomes more evident when looking at the susceptibility M/H in Fig. 4(b). Only in fields above 10 T the susceptibility is inversely proportional to the external magnetic field as indicated by the dotted line in Fig. 4(b). Below H_{c3} the experimentally observed susceptibility starts to deviate from saturation and exhibits a pronounced anomaly at H_{c2}.

We will now discuss the possible origin of the temperature- and field-dependent anomalies, which are summarized in the H-T phase diagram for $ZnCr_2Se_4$ shown in Fig. 5. The sound velocity and attenuation are sensitive to both structural and

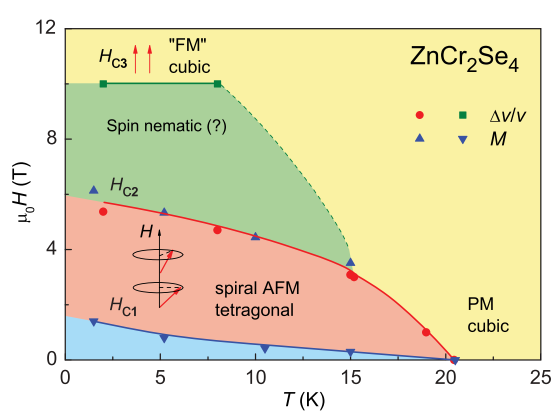

FIG. 5. (Color online) H-T phase diagram for $ZnCr_2Se_4$. Phase below H_{c1} corresponds to a multidomain state. Phases PM and FM correspond, respectively, to the paramagnetic and magnetic field-induced ferromagnetic states. The boundary between the proposed spin nematic and PM phases at temperatures above 8 K is drawn arbitrarily.

magnetic changes via magnetoelastic coupling, which very often prohibits a clear separation of the two contributions. Note that colossal magnetostriction in $ZnCr_2Se_4$ revealed by earlier studies[12] is by two orders of value lower than the changes in the sound velocity and therefore has only a minor contribution to observed effects. The structural transformation from the cubic to tetragonal state at T_N in $ZnCr_2Se_4$ cannot be attributed to a conventional Jahn-Teller effect related to orbital degeneracy because of the half filled t_{2g} shell of the Cr^{3+} ions. Infrared optical spectroscopy studies indicated that the structural transformation at T_N is coupled to spin ordering via the spin-Jahn-Teller effect.[32] The observed features in the sound velocity and attenuation indeed show a clear correlation with the changes in the magnetization. In the magnetically ordered state, the application of the magnetic field in the ⟨001⟩ direction deflects the spins from the (001) planes forming a cone arrangement. With increasing field, the cone angle decreases. At the same time the screw angle between the spins of adjacent (001) planes is expected to change only little with magnetic field, which is supported by neutron-diffraction studies, where a small change of the screw angle from 42° to 39° was found with increasing temperature from 2 K up to T_N.[30] Therefore, the variation of the sound velocity with increasing field up to 5.4 T (at 2 K) can be attributed mainly to a reduction of the cone angle in the spiral AFM phase between H_{c1} and H_{c2}. Above 5.4 T, the magnetization still shows a slight increase indicating that the noncollinear spin configuration might not yet be fully suppressed and the fully polarized ferromagnetic spin alignment is reached only above 10 T. We want to mention that also the dielectric polarization in $ZnCr_2Se_4$ shows a complex magnetic field dependence with a maximum at about 3 T and a complete vanishing at 6.3 T,[19] which might be related to remainders of noncollinear magnetic domains above H_{c2}. We assume that above ∼6.4 T the magnetic field also restores cubic symmetry, i.e., the field overrules the magnetoelastic coupling. This is in agreement with the energy scale set by the experimentally observed splitting of 3 cm^{-1} ∼ 6.4 T of the infrared active phonons due to spin-phonon coupling.[23,32] The splitting itself is not resolvable anymore in a magnetic field of 7 T.[32] Similarly, the estimates of the leading antiferromagnetic exchange constant $J_3 \approx 8$ K ∼ 12 T identify an energy scale necessary to reach full spin polarization.[33]

The disappearance of the dielectric polarization in a field notably less than the saturation field needs additional considerations for the origin of the multiferroic behavior in $ZnCr_2Se_4$ beyond the spin-current model. In the range 7 T < H < 10 T the sound velocity exhibits a first plateau indicating a metastable magnetostructural phase. Above 10 T both an increase in the elastic stiffness and a broad maximum in the attenuation of the order of 3 dB/cm [see inset in Fig. 3(b)] appear and then the ultrasound parameters seem to saturate concomitantly to the magnetization.

Finally, we would like to comment on the relation to the recently reported H-T phase diagram of the spinel $ZnCr_2S_4$.[15] First, the spiral spin arrangement in $ZnCr_2Se_4$ is similar to the one induced by a magnetic field in the range 27 T < H < 37 T (at 1.5 K) in $ZnCr_2S_4$. For larger fields the sound velocity and the attenuation in $ZnCr_2S_4$ behave qualitatively similar as in $ZnCr_2Se_4$, with a plateau being reached in a metastable possible cubic phase and a further increase and saturation when the magnetization corresponds to an almost complete ferromagnetic polarization. Therefore, we conclude that the presence of Se ions instead of S is comparable to the effects of an external magnetic field. In both compounds the region where the sound velocity exhibits a plateau is not fully understood. It seems to be a metastable magnetoelastic phase without complete spin polarization. This might be either due to the presence of not completely aligned domains or it might be related to a nematic spin ordering, i.e., a phase in which the transverse spin components order close to the saturating external field. Spin nematic behavior since long has been proposed theoretically[34] and has recently been experimentally identified in the frustrated AFM chain compound $LiCuVO_4$ with incommensurate spiral spin order.[35] Thus far, however, the actual spin arrangement of this state is unclear and demands for additional neutron-diffraction studies. Also, x-ray experiments with synchrotron radiation under magnetic field would be necessary to get a definite answer on the symmetry change at high fields in $ZnCr_2Se_4$.

IV. CONCLUSIONS

In conclusion, ultrasound studies in magnetic fields of the bond-frustrated spinel $ZnCr_2Se_4$ reveal significant anomalies in the sound velocity and attenuation at the antiferromagnetic transition indicating strong magnetoelastic coupling. Magnetic fields are shifting the sharp anomalies in the sound velocity and attenuation to lower temperatures. The anomalies in the magnetic field dependence of the sound velocity and attenuation are correlated with the changes in the magnetization. The first plateau in the sound velocity observed in fields between 7 and 10 T is suggested to be related to changes of the crystal symmetry from tetragonal to cubic. The second plateau observed in the sound velocity at fields above 10 T corresponds to a state with increased stiffness and is related to a state with fully polarized magnetic moment.

ACKNOWLEDGMENTS

The authors are thankful to D. Vieweg for experimental support. This research has been supported by the DFG via TRR 80 (Augsburg-Munich) and FOR 960 (Quantum Phase Transitions), LE 967/6-1 (Braunschweig), and by EuroMagNET II under Contract No. 228043.

[1] S.-H. Lee, C. Broholm, W. Ratcliff, G. Gasparovic, Q. Huang, T. H. Kim, and S.-W. Cheong, Nature (London) **418**, 856 (2002).

[2] P. G. Radaelli, Y. Horibe, M. J. Gutmann, H. Ishibashi, C. H. Chen, R. M. Ibberson, Y. Koyama, Y.-S. Hor, V. Kiryukhin, and S.-W. Cheong, Nature (London) **416**, 155 (2002).

[3]M. Schmidt, W. Ratcliff, P. G. Radaelli, K. Refson, N. M. Harrison, and S.-W. Cheong, Phys. Rev. Lett. **92**, 056402 (2004).
[4]S. Kondo, D. C. Johnston, C. A. Swenson, F. Borsa, A. V. Mahajan, L. L. Miller, T. Gu, A. I. Goldman, M. B. Maple, D. A. Gajewski, E. J. Freeman, N. R. Dilley, R. P. Dickey, J. Merrin, K. Kojima, G. M. Luke, Y. J. Uemura, O. Chmaissem, and J. D. Jorgensen, Phys. Rev. Lett. **78**, 3729 (1997).
[5]A. Krimmel, A. Loidl, M. Klemm, S. Horn, and H. Schober, Phys. Rev. Lett. **82**, 2919 (1999).
[6]V. Fritsch, J. Hemberger, N. Büttgen, E.-W. Scheidt, H.-A. Krug von Nidda, A. Loidl, and V. Tsurkan, Phys. Rev. Lett. **92**, 116401 (2004).
[7]R. Fichtl, V. Tsurkan, P. Lunkenheimer, J. Hemberger, V. Fritsch, H.-A. Krug von Nidda, E.-W. Scheidt, and A. Loidl, Phys. Rev. Lett. **94**, 027601 (2005).
[8]V. Tsurkan, V. Fritsch, J. Hemberger, H.-A. Krug von Nidda, N. Büttgen, D. Samusi, S. Körner, E.-W. Scheidt, S. Horn, R. Tidecks, and A. Loidl, J. Phys. Chem. Solids **66**, 2036 (2005).
[9]S.-H. Lee, C. Broholm, T. H. Kim, W. Ratcliff, II, and S-W. Cheong, Phys. Rev. Lett. **84**, 3718 (2000).
[10]A. B. Sushkov, O. Tchernyshyov, W. Ratcliff, S.-W. Cheong, and H. D. Drew, Phys. Rev. Lett. **94**, 137202 (2005).
[11]J. Hemberger, T. Rudolf, H.-A. Krug von Nidda, F. Mayr, A. Pimenov, V. Tsurkan, and A. Loidl, Phys. Rev. Lett. **97**, 087204 (2006).
[12]J. Hemberger, H.-A. Krug von Nidda, V. Tsurkan, and A. Loidl, Phys. Rev. Lett. **98**, 147203 (2007).
[13]H. Ueda, H. A. Katori, H. Mitamura, T. Goto, and H. Takagi, Phys. Rev. Lett. **94**, 047202 (2005).
[14]M. Matsuda, H. Ueda, A. Kikkawa, Y. Tanaka, K. Katsumata, Y. Narumi, T. Inami, Y. Ueda, and S.-H. Lee, Nat. Phys. **3**, 397 (2007).
[15]V. Tsurkan, S. Zherlitsyn, V. Felea, S. Yasin, Yu. Scourski, J. Deisenhofer, H.-A. Krug von Nidda, P. Lemmens, J. Wosnitza, and A. Loidl, Phys. Rev. Lett. **106**, 247202 (2011).
[16]J. Hemberger, P. Lunkenheimer, R. Fichtl, H.-A. Krug von Nidda, V. Tsurkan, and A. Loidl, Nature (London) **434**, 364 (2005).
[17]M. Mostovoy, Phys. Rev. Lett. **96**, 067601 (2006).
[18]S. Weber, P. Lunkenheimer, R. Fichtl, J. Hemberger, V. Tsurkan, and A. Loidl, Phys. Rev. Lett. **96**, 157202 (2006).
[19]H. Murakawa, Y. Onose, K. Ohgushi, S. Ishiwata, and Y. Tokura, J. Phys. Soc. Jpn. **77**, 043709 (2008).
[20]Y. J. Choi, J. Okamoto, D. J. Huang, K. S. Chao, H. J. Lin, C. T. Chen, M. van Veenendaal, T. A. Kaplan, and S.-W. Cheong, Phys. Rev. Lett. **102**, 067601 (2009).
[21]T. Kimura and Y. Tokura, J. Phys.: Condens. Matter **20**, 434204 (2008).
[22]Y. Tokura and S. Seki, Adv. Mater. **22**, 1554 (2010).
[23]T. Rudolf, Ch. Kant, F. Mayr, M. Schmidt, V. Tsurkan, J. Deisenhofer, and A. Loidl, Eur. Phys. J. B **68**, 153 (2009).
[24]Ch. Kant, J. Deisenhofer, T. Rudolf, F. Mayr, F. Schrettle, A. Loidl, V. Gnezdilov, D. Wulferding, P. Lemmens, and V. Tsurkan, Phys. Rev. B **80**, 214417 (2009).
[25]Ch. Kant, M. Schmidt, Zhe Wang, F. Mayr, V. Tsurkan, J. Deisenhofer, and A. Loidl, Phys. Rev. Lett. **108**, 177203 (2012).
[26]F. K. Lotgering, *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and the Physical Society, London, 1965), p. 533.
[27]R. Plumier, J. Phys. **27**, 213 (1966).
[28]R. Kleinberger and R. de Kouchkovsky, C. R. Acad. Sci. Paris Ser. B **262**, 628 (1966).
[29]M. Hidaka, N. Tokiwa, M. Fujii, S. Watanabe, and J. Akimitsu, Phys. Status Solidi B **236**, 9 (2003).
[30]F. Yokaichiya, A. Krimmel, V. Tsurkan, I. Margiolaki, P. Thompson, H. N. Bordallo, A. Buchsteiner, N. Stusser, D. N. Argyriou, and A. Loidl, Phys. Rev. B **79**, 064423 (2009).
[31]B. Wolf, B. Lüthi, S. Schmidt, H. Schwenk, M. Sieling, S. Zherlitsyn, and I. Kouroudis, Physica B **294-295**, 612 (2001).
[32]T. Rudolf, Ch. Kant, F. Mayr, J. Hemberger, V. Tsurkan, and A. Loidl, Phys. Rev. B **75**, 052410 (2007).
[33]A. N. Yaresko, Phys. Rev. B **77**, 115106 (2008).
[34]P. Chandra, P. Coleman, and A. I. Larkin, J. Phys.: Condens. Matter **2**, 7933 (1990).
[35]L. E. Svistov, T. Fujita, H. Yamaguchi, S. Kimura, K. Omura, A. Prokofiev, A. I. Smirnov, Z. Honda, and M. Hagiwara, JETP Lett. **93**, 21 (2011).