Letter

Unusual field-induced spin reorientation in $FeCr_2S_4$: Field tuning of the Jahn-Teller state

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(Received 4 December 2020; accepted 29 June 2021; published 16 July 2021)

The multiferroic spinel $FeCr_2S_4$ is a benchmark material for exploring the competition of spin-orbit (SO) and Jahn-Teller (JT) coupling. Our magnetic and thermodynamic studies of stoichiometric single-crystalline samples evidence a magnetic-field-induced spin-reorientation transition in the cooperative JT state below 10 K. At 2 K, at a critical magnetic field of 4.5 T, the magnetization measured along the hard magnetization axis ⟨111⟩ manifests a jump to the fully saturated state accompanied by a steplike decrease of the sound velocity and an abrupt increase of the magnetostriction. All these quantities reveal a hysteretic behavior pointing towards a first-order magnetostructural transformation. Below the JT transition, the specific heat shows a complex behavior upon the application of magnetic fields depending on the crystallographic directions. The observed reduction by 20% of the magnetic anisotropy below the JT transition is attributed to the competition of the SO and JT interactions tuned by external magnetic fields. The concomitant change of the structural symmetry results in a change of the splitting of the lowest levels of the ^5E doublet of the tetrahedrally coordinated Fe^{2+} ions.

DOI: 10.1103/PhysRevB.104.L020410

Recently, *d*-electron systems with strong spin-orbit (SO) interaction came into the focus of experimental and theoretical condensed-matter physics. A number of exotic phases, such as quantum spin-liquids and spin-orbital liquids, were predicted due to the competition of SO coupling with crystal-field and magnetic-exchange (ME) interactions [1,2]. In 3*d* magnetic systems, SO interaction is weaker than the magnetic exchange. However, it contributes significantly to their magnetic, elastic, optical, and transport properties, governing magnetocrystalline anisotropy, magnetostriction, magneto-optical Kerr effect, spontaneous magnetoresistance, anomalous Hall, and Nernst effects.

Magnetic materials exhibiting a Jahn-Teller (JT) transition provide an additional possibility to realize unconventional states due to the competition of JT coupling with other types of interactions of comparable strength, e.g., SO and ME [3]. However, in most of the known magnetic JT systems the JT ordering takes place at temperatures far above the magnetic ordering temperature. Highly anisotropic magnets, where orbital ordering sets in deep within a long-range magnetically ordered phase, are rare.

One particular example is the cubic ferrimagnet $FeCr_2S_4$. It belongs to a family of ternary chalcogenide spinels that show complex physics driven by the interplay of spin, charge, orbital, and lattice degrees of freedom [4]. $FeCr_2S_4$ orders below 170 K with a collinear arrangement of the spins of the tetrahedrally coordinated Fe^{2+} ions antiferromagnetically coupled with the spins of the octahedrally coordinated Cr^{3+} ions [5]. Below 50 K, the collinear spin structure transforms into an incommensurate spin spiral, which remains the stable configuration towards the lowest temperature [6,7]. $FeCr_2S_4$ shows a significant SO coupling, manifesting a remarkably high magnetocrystalline anisotropy, which is attributed solely to tetrahedral Fe^{2+} ions being in a $3d^6$ state with $S = 2$ [8,9]. In a cubic crystal field the ^5D free-ion level of the Fe^{2+} ions splits into a ^5E ground state and a ^5T excited state with an energy separation $\Delta_{CF} \approx 2500\ cm^{-1}$ [10–12] [see Fig. 3(a)]. The ^5E state is split by exchange interactions into five equidistant doublets spaced by about $230\ cm^{-1}$ as estimated from the Curie temperature. The lowest *E* doublet is further split by the second-order SO and spin-spin interactions into θ and ϵ components with the energy separation $2\delta = 6\lambda^2/\Delta_{CF}$, which is less than $50\ cm^{-1}$ [13]. Here λ is the strength of the SO interaction. The combined action of the ME and SO interactions induces an anisotropic splitting of the ground-state doublet and confines the magnetization to the ⟨100⟩ crystallographic direction, being the easy axis of magnetization. The hard axis is ⟨111⟩ and the lowest levels of the ^5E doublet in this direction are almost degenerate [14,15].

A well-known peculiarity of Fe^{2+} ions is their JT activity, which was established in $FeCr_2S_4$ utilizing Mössbauer

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measurements by observation of a quadrupole-line splitting and a steplike change of the electric-field gradient at the Fe sites at 10 K [16,17]. This change of the local symmetry at the Fe sites was attributed to a cooperative JT effect [13,18] and concomitant orbital ordering (OO) [17,19]. The JT effect results in a λ-like anomaly in the specific heat at 10 K [20]. $FeCr_2S_4$ is a role model where the interplay of strong SO coupling with cooperative JT phenomena is anticipated to induce a unconventional magnetostructural anomaly.

Although $FeCr_2S_4$ was widely studied over the last 50 years, its magnetic behavior in the orbital-liquid and orbitally ordered states is still far from being well understood [21–26]. Experimental study of the correlations between SO and JT couplings is complicated by the high sensitivity of the orbital state of $FeCr_2S_4$ to deviations from the stoichiometry [20,27,28], which can suppress orbital ordering [28–30]. The very recent reports on the multiferroicity [31,32] and optical studies in the THz and far-infrared frequency range [12,33] of stoichiometric $FeCr_2S_4$ have provided clear evidence of a lowering of the lattice symmetry in the orbitally ordered phase. These findings motivated the present study aimed to provide insight into the competition of JT and SO couplings in $FeCr_2S_4$ and their effect on the macroscopic magnetic properties, particularly on magnetic anisotropy. Note that so far, the orbitally ordered ground state was reported only in polycrystalline $FeCr_2S_4$, in which magnetic anisotropy effects are averaged and therefore hardly discernible.

In this paper we report an experimental study of magnetic and thermodynamic properties of $FeCr_2S_4$ single crystals that manifest a sharp λ-like anomaly in the specific heat at the JT transition. Within the JT ordered phase we identified an unusual magnetostructural phase transition: when measured along the hard magnetization axis, at a certain critical field the magnetization exhibits a jump towards complete saturation, which is accompanied by steplike anomalies in the ultrasound velocity and magnetostriction.

Figure 1(a) shows the temperature-dependent magnetization M measured in a magnetic field of 10 mT and specific heat in the representation C/T measured in zero field. These data illustrate generic features at the magnetic and structural transitions in this compound: a steplike increase of M and a λ-like anomaly in C/T at the Curie temperature T_C, a spikelike anomaly in M at the temperature T_m, where the incommensurate spiral spin order is established [6], indicated by a splitting of zero-field-cooled and field-cooled magnetization, and finally, a second sharp λ-like anomaly in C/T at $T_{OO} = 8.9$ K, indicating the cooperative JT transition.

Figure 1(b) shows the specific heat C/T at temperatures below 12 K. The application of magnetic fields along the ⟨111⟩ axis reveals a complex behavior: first, in fields up to 7 T, the maximum in C is shifted to lower temperatures ($T_{OO} = 8.54$ K), but then, for further increasing field up to 9 T, the λ-like anomaly becomes strongly shifted towards higher temperatures ($T_{OO} = 9.4$ K). At the same time, magnetic fields applied along the easy magnetization direction ⟨100⟩ do not influence the specific heat. Such a surprising anisotropic behavior of the thermodynamic properties of $FeCr_2S_4$ reveals the influence of the detected field-induced spin-reorientation (FISR) transition described in detail below. It is important to note that samples with suppressed JT transition (without the λ-like anomaly in C below 10 K) also show strongly anisotropic magnetic properties but, in contrast, do not exhibit such a FISR transition at high fields [9,22,28,34].

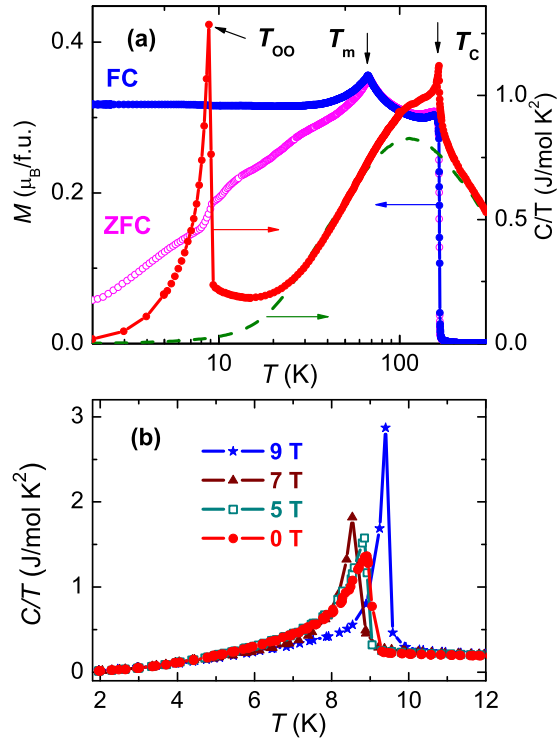

FIG. 1. (a) Temperature-dependent magnetization M (left scale) measured in an external magnetic field of 10 mT and zero-field specific heat plotted as C/T vs T (right scale) for single-crystalline $FeCr_2S_4$. Vertical arrows mark the Curie temperature $T_C = 165.5$ K, the Jahn-Teller transition at $T_{OO} = 8.9$ K, and the temperature $T_m = 67$ K indicating deviations from collinear spin order via the appearance of irreversibility between the zero-field-cooled (ZFC) and field-cooled (FC) magnetization. The green dashed line shows the specific heat of the spinel $ZnSc_2S_4$. (b) Temperature-dependent specific heat C/T vs T measured in various external magnetic fields up to 9 T applied along the ⟨111⟩ axis in the temperature range relevant for orbital ordering.

The main results of the present study are illustrated in Fig. 2. Figure 2(a) shows the magnetization $M(H)$ measured at 2 K along three main cubic crystallographic directions. In fields below 4 T, the $M(H)$ curves are prototypical for highly anisotropic ferro(ferri)magnets, with the easy axis of magnetization along the ⟨100⟩, the medium axis along the ⟨110⟩, and the hard axis along the ⟨111⟩ directions. In fields above 4.5 T, $M(H)$ measured along ⟨111⟩ reveals a sudden jump to magnetization saturation characteristic for the easy magnetization direction ⟨100⟩. This FISR transition exhibits a pronounced hysteresis on increasing and decreasing fields, indicating a first-order magnetostructural phase transformation. The jump of the magnetization with strong hysteretic behavior and the absence of a hysteresis of M below a field of 4 T indicate a magnetostructural transformation induced by additional splitting of the energy levels by magnetic field. For H applied along the ⟨110⟩ axis, the hysteretic transition in $M(H)$ at 2 K takes place at a higher field of 5.5 T. On increasing temperatures $T > 2$ K, the FISR transition shifts

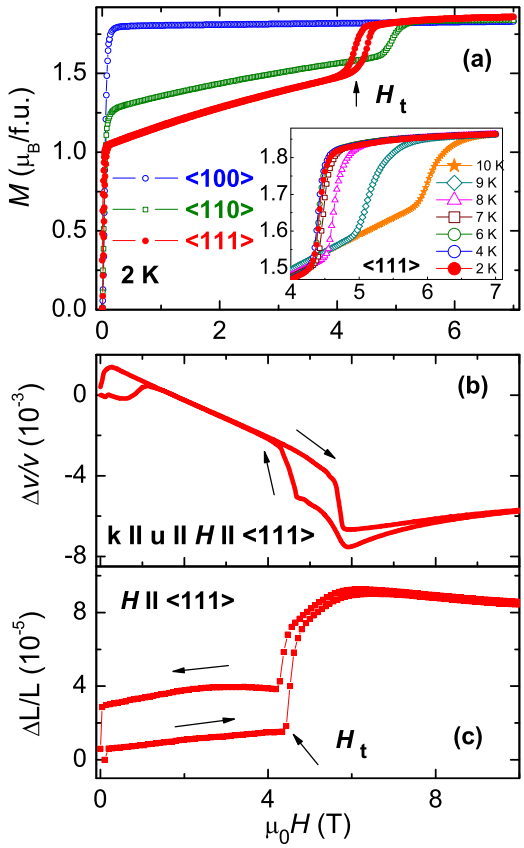

FIG. 2. (a) Magnetization curves in $FeCr_2S_4$ at 2 K measured along the crystallographic directions ⟨100⟩, ⟨110⟩, and ⟨111⟩. The inset shows the temperature evolution of the FISR transition along the ⟨111⟩ axis. (b) Magnetic-field dependence of the relative change of the sound velocity, $\Delta v/v$, of the longitudinal waves propagating along the ⟨111⟩ axis at 1.4 K. (c) Magnetic-field dependence of the normalized change of the sample length $\Delta L/L$ measured along the ⟨111⟩ axis at 1.5 K. Arrows mark the FISR transition field, H_t, and directions of the field sweeps. Note different scales for the horizontal axes in panels (a), (b), and (c).

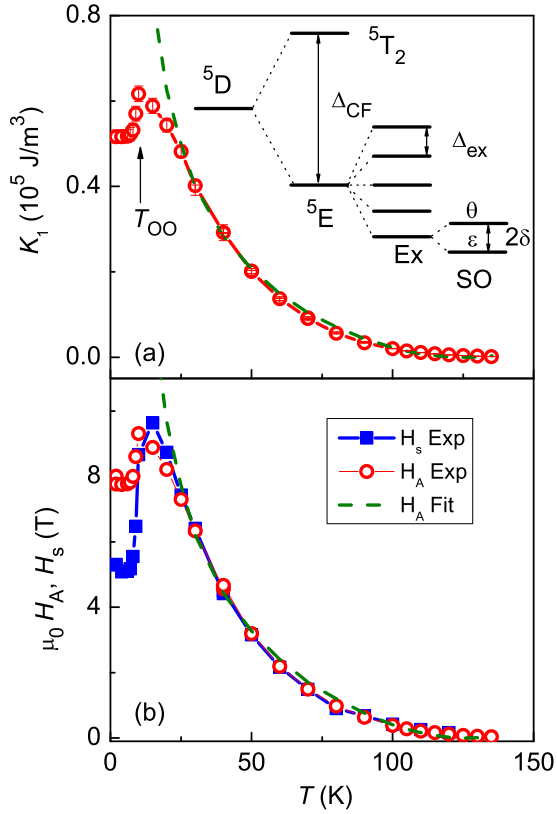

FIG. 3. (a) Temperature dependence of the anisotropy constant K_1 for $FeCr_2S_4$: the experimental data are shown by open circles. Last eight points at high temperature are derived from the ESR measurements. Inset shows the splittings of the levels of the tetrahedrally coordinated Fe^{2+} ion due to crystal-field (CF), exchange (EX), and SO interactions. (b) Temperature dependence of the anisotropy field $H_A = 2K_1/M_s$ and of the saturation field H_s extracted from the magnetization and ESR data. Dashed green lines in both frames show the fits to the experimental data within the single-ion model.

to higher fields with concomitant reduction of the hysteresis [see the inset of Fig. 2(a)]. Above 10 K, the FISR transition is smeared out and not resolved anymore.

In Fig. 2(b), the relative change of the sound velocity, $\Delta v/v$, for longitudinal ultrasound waves propagating along the ⟨111⟩ at 1.4 K is shown as a function of magnetic field applied along the same direction. For the field up-sweep, above 1 T, $\Delta v/v$ decreases linearly up to 4.3 T, and at higher fields it manifests a sharp drop with a kink in a field of 5.6 T, where the magnetization reaches saturation [see inset of Fig. 2(a)]. For the down-sweep, $\Delta v/v$ shows a pronounced hysteresis with a two-step recovery to its initial value of the up-sweep, confirming the first-order magnetostructural transformation revealed in the magnetization.

Figure 2(c) presents the magnetic-field dependence of the normalized change of the sample length, $\Delta L/L$, measured along the ⟨111⟩ axis at 1.5 K. $\Delta L/L$ increases linearly up to a field of 4.5 T, followed by a steplike positive jump at the FISR transition. Above the transition, $\Delta L/L$ shows a broad maximum with a tendency to saturation and a slight decrease at the highest fields. The overall increase of $\Delta L/L$ with magnetic field amounts to 10^{-4}, indicating substantial magnetoelastic coupling. At the FISR transition the magnetostriction also evidences the strong hysteretic behavior similar to the ultrasound velocity and magnetization.

Figure 3(a) shows the temperature dependence of the first anisotropy constant K_1 calculated from the $M(H)$ curves using an "area method" following Ref. [35] for the range 2–120 K and from the electron spin resonance (ESR) data for the range 100–140 K (see [36]). Below T_C, K_1 reveals a continuous increase on decreasing temperatures down to 10 K, where it develops a maximum close to the temperature of the JT transition T_{OO}. Below T_{OO}, K_1 is reduced by approximately 20%. Such a strong reduction of the anisotropy suggests that the low-temperature and high-temperature phases exhibit a different level splitting, corroborating the fact that these states possess different crystallographic structures, in agreement with recent optical studies of stoichiometric $FeCr_2S_4$ [12,33].

Figure 3(b) compares the temperature dependences of the anisotropy field $H_A = 2K_1/M_s$ and the saturation field H_s extracted from our magnetization and ESR measurements. Both quantities continuously increase on decreasing temperatures

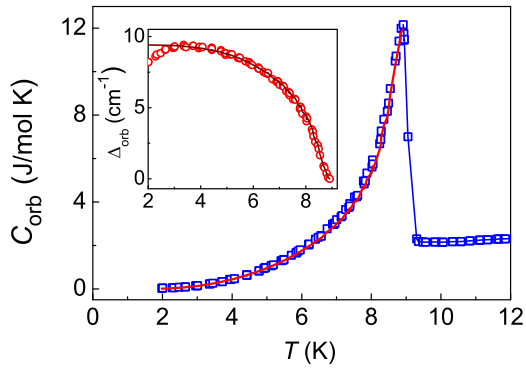

FIG. 4. Temperature dependence of the orbital contribution to specific heat C_{orb} for $FeCr_2S_4$ measured in zero field. Inset shows the temperature dependence of the JT splitting Δ. Solid lines in the main frame and in the inset show the fits to the experimental specific heat C_{orb} and splitting parameter Δ_{orb}.

below T_C and reveal a well-defined jumplike decrease that sets in at around 10 K. The remarkable correlation between H_A and H_s indicates dominant SO interaction at high temperatures, while a significant difference between them below T_{OO} supports the scenario of the competition of the SO and JT interactions, resulting in reduction of the magnetocrystalline anisotropy at the JT transition in $FeCr_2S_4$.

The reduction of the magnetocrystalline anisotropy below T_{OO}, found here in stoichiometric $FeCr_2S_4$ single crystals, we interpret as being due to a change of the splitting of the lowest levels of the ^5E doublet of the tetrahedrally coordinated Fe^{2+} ions. In the temperature range above the JT correlations $T_m < T < T_C$, $FeCr_2S_4$ can be considered as a conventional highly anisotropic ferromagnet. We treated our experimental data using a crystal-field model proposed in Refs. [8,9,15], which relates the anisotropy constant K_1 and the splitting of the lowest doublet level due to exchange and SO interactions (see for details [36]). A fit to the experimental data for K_1 within this model is shown by the dashed line in Fig. 3(a) with a splitting $\Delta_{SO} = 7.4$ cm^{-1}. Below 20 K, the fit deviates significantly from the experimental data, suggesting the reduction of the level splitting. We noticed, however, that the value of splitting evaluated from the fit is by a factor of 1.5–2.3 lower than the values of splitting due to SO interaction reported for $FeCr_2S_4$ [9,13] and for Fe^{2+} impurities in $CdCr_2S_4$ [15,37]. The reason of such a discrepancy can be related to the difference in the evaluation of the temperature dependence of the spin moment in our treatment and in Refs. [9,13,15,37], which has significant influence on the value of the splitting. This problem requires further analysis.

To provide further insight into the splitting of the ^5E doublet levels below the JT transition we analyzed the specific heat C_{orb} related to orbital ordering, which was calculated by subtracting the lattice contribution C_{lat} from the total specific heat. For C_{lat} we used the data for the nonmagnetic spinel $ZnSc_2S_4$ with a molar mass differing only by 1.6% compared to that of $FeCr_2S_4$, which is shown by the dashed line in Fig. 1(a). In Fig. 4 the temperature dependence of C_{orb} is shown at low temperatures for zero magnetic field. Below 15 K, C_{orb} exhibits a temperature-independent term followed by a sharp anomaly at T_{OO} and an exponential decrease towards the lowest temperature. The temperature dependence of C_{orb} was treated within a mean-field model for a two-level system, in which a gap Δ is opened at T_{OO}, providing a steplike increase of C_{orb} at the transition temperature and an exponential decrease towards 0 K. The model assumes that Δ varies with temperature according to $\Delta = \Delta_0 \tanh(\Delta T_{OO}/\Delta_0 T)$, where Δ_0 is the gap value at 0 K. The mean-field model for description of the specific heat in $FeCr_2S_4$ was discussed earlier in Ref. [23]. The solid line in the main frame of Fig. 4 shows the fit to C_{orb} below T_{OO} with the gap $\Delta_0 = 9.4$ cm^{-1}. The obtained value of Δ_0 agrees well with that for stoichiometric polycrystalline $FeCr_2S_4$ [23]. The temperature dependence of Δ_{orb} is shown in the inset of Fig. 4. It describes well the experimental data within the whole measured temperature range, except the temperatures below 3 K. Thus, from the above analysis we assume that the JT effect can produce a significant splitting of the lowest ^5E doublet levels below the JT transition comparable with the splitting due to SO interaction.

The external magnetic field clearly has an important role in tuning the competition between SO and JT interactions, and the Zeeman splitting of the lower ^5E doublet levels for $\langle 111 \rangle$ direction must be accounted. The nonmonotonic temperature shift of the λ-like anomaly in the specific heat at T_{OO} [Fig. 1(b)] and the shift to higher fields of the FISR transition with increasing temperature [Fig. 2(a)] in the orbitally ordered phase reflect the complex interplay of the spin, orbital, and structural degree of freedom. The microscopic mechanisms that lead to such an exotic behavior of the magnetic and thermodynamic properties as well as the symmetry of the JT ground state of stoichiometric $FeCr_2S_4$ require further experimental and theoretical studies.

The competing JT and SO interactions seem to favor different orbital ground states. This conclusion corroborates the results of Refs. [6,15,16], which reported a significant change in the quadrupole interactions identified by a change of sign and reorientation of the electric-field gradient below 10 K in Mössbauer experiments on stoichiometric $FeCr_2S_4$ polycrystals. This implies the reduction of the splitting and even the inversion of the components of the ground state ^5E doublet level of the Fe^{2+} ions below the orbital-ordering temperature as proposed in Ref. [6].

In conclusion, the present magnetic, thermodynamic, ultrasound, and magnetostriction studies in magnetic fields up to 14 T evidence an unconventional magnetic-field-induced spin-reorientation transition in stoichiometric single-crystalline $FeCr_2S_4$ with an orbitally ordered ground state. At a certain critical field, the magnetization measured along the direction of hard magnetization $\langle 111 \rangle$ reveals a jump towards full saturation, which is accompanied by a steplike decrease of the velocity of the longitudinal acoustic mode. Magnetostriction measurements confirm the magnetostructural nature of this first-order phase transformation. Our results emphasize the important role of the orbital ordering and evidence the remarkable and strong competition between JT and SO interactions. The reduction of the magnetic anisotropy in the cooperative JT state is attributed to changes in the splitting of the lowest levels of the ^5E ground-state doublet of the tetrahedrally coordinated Fe^{2+} ions due to reduction of the lattice symmetry.

We acknowledge experimental support from Dana Vieweg (SQUID measurements) and Thomas Wiedenmann (thermal expansion). This work was supported by the Deutsche Forschungsgemeinschaft (DFG) through the Transregional Research Collaboration TRR 80 (Augsburg, Munich, and Stuttgart, Project No. 107745057), through SFB 1143 (Dresden), the Würzburg-Dresden Cluster of Excellence on Complexity and Topology in Quantum Matter-ct.qmat (EXC 2147, Project No. 390858490), and by the project ANCD 20.80009.5007.19 (Moldova). We acknowledge support by HLD at HZDR, a member of the European Magnetic Field Laboratory (EMFL).

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