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Magnetic anomaly around orbital ordering in $FeCr_2S_4$

Chen Shen,[1] Zhaorong Yang,[1,a)] Ran Tong,[1] Zhenfa Zi,[1] Wenhai Song,[1] Yuping Sun,[1] Li Pi,[2] and Yuheng Zhang[2]
[1]*Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, People's Republic of China*
[2]*High Magnetic Field Laboratory, Chinese Academy of Sciences, University of Science and Technology of China, Hefei 230026, People's Republic of China*

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For polycrystalline $FeCr_2S_4$, temperature dependence of low-field magnetization shows a step-like transition around orbital ordering temperature $T_{oo} \sim 9$ K. In this paper, the origin of the magnetic anomaly has been studied. We show that, with increasing magnetic field, the step-like anomaly in *M–T* curve is gradually suppressed. However, the external magnetic field up to 5 T has no evident influence on orbital ordering transition as revealed by specific heat measurements. T_{oo} was increased when an ultrahigh magnetic field, e.g., 14 T, has been applied. Being contrary to the inert response to magnetic field, the T_{oo} is sensitive to the variation of external pressure. *M(H)* curves measured at different temperatures suggest that magnetic anisotropy changes oppositely going across T_{oo}. By considering the variation of magnetocrystalline symmetry induced by orbital ordering, the magnetic anomaly around T_{oo} has been explained. © *2011 American Institute of Physics*. [doi:10.1063/1.3562449]

The role of orbital degrees of freedom in determining the physical properties of correlated electron system has been emphasized in the past few years.[1,2] Due to its strong coupling with spin, charge and lattice degrees of freedom, the change of orbital degrees of freedom is normally accompanied by the variation of the others, which contributes to many fascinating phenomena. $FeCr_2S_4$ is a typical example involving the interplay of all the degrees of freedom. This material not only shows fascinating physical effects, e.g., colossal magnetoresistance and gigantic Kerr rotation, but also displays abnormal low-field magnetic behavior as well as complex orbital state.[3–11] For polycrystalline sample, temperature dependence of low-field magnetization shows a step-like transition around orbital ordering temperature $T_{oo} \sim 9$ K.[7,11] However, in single crystal samples, the step-like transition disappears and the orbital ordering state is replaced by orbital glass.[7,11] As the magnetic anomaly is a polycrystalline sample and is concomitant of orbital ordering, the origin was simply attributed to orbital degrees of freedom, although the detail is still unclear.[7]

In this paper, the influence of external magnetic field and pressure on both the magnetic anomaly and orbital ordering transition of polycrystalline $FeCr_2S_4$ has been investigated. We show that with increasing magnetic field, the step-like anomaly in magnetization below 9 K is gradually suppressed. The external magnetic field up to 5 T has no influence on the orbital ordering transition, whereas T_{oo} is sensitive to the variation of external pressure. By considering the changes of magnetocrystalline symmetry below T_{oo}, the magnetic anomaly has been explained qualitatively.

The polycrystalline $FeCr_2S_4$ samples were prepared by a standard solid-state synthesis method.[9] Structure and phase purity were examined by an x-ray power diffraction (XRD) method, with Cu $K\alpha$ radiation at room temperature. The XRD analysis reveals that the sample is single phase with spinel structure. Magnetization measurements were performed with a commercial superconducting quantum interference device magnetometer MPMS-XL (Quantum Design) in the temperature range from 4 to 200 K and at magnetic fields up to 4.5 T. The application of pressure was performed in an Easylab Mcell 10 Pressure cell. The heat capacity was investigated by a thermal relaxation method using a physical property measurement system (Quantum Design PPMS) in the temperature range of 4–20 K at different applied magnetic fields.

Figures 1(a)–1(d) display the magnetization as a function of temperature obtained in zero-field-cooled (ZFC) and field-cooled (FC) processes under different applied fields for polycrystalline $FeCr_2S_4$. The insets show enlarged views of the magnetization around 9 K. As seen from Fig. 1(a), at a low magnetic field of $H = 0.005$ T and with decreasing temperature below the Curie temperature, the $FeCr_2S_4$ first shows irreversible behavior between the ZFC and FC curves and then a cusp-like anomaly around 70 K, which was explained in our previous work, as resulting from the abrupt increase of magnetic anisotropy below 70 K.[10] With further decreasing temperature, the magnetization displays a step-like downturn (ZFC) or upturn (FC) transition around 9 K, corresponding to the onset of orbital ordering.[7] As the magnetic field is increased, as shown in Figs. 1(b)–1(d), the gap between the ZFC and FC curves is gradually reduced, and the downturn transition in ZFC changes to an upturn at $H = 0.5$ T. The step-like anomaly in the ZFC and FC curves is being suppressed gradually with further increasing magnetic field. At $H = 4.5$ T, the anomaly is completely suppressed, where FC and ZFC almost coincide with each other.

Due to the orbital ordering transition around 9 K, one can naturally suppose that the magnetic anomaly comes from the orbital degrees of freedom itself as mentioned earlier.[7] As the magnetic anomaly can be suppressed by magnetic field,

a)Author to whom correspondence should be addressed. Electronic mail: zryang@issp.ac.cn.

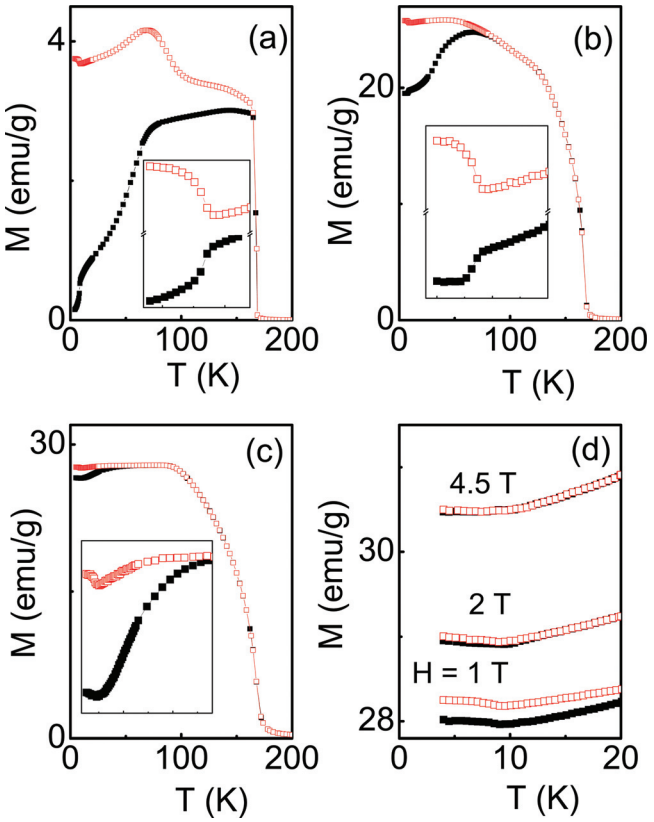

FIG. 1. (Color online) Zero-field cooling (solid circle) and field cooling (open circle) magnetization as a function of temperature for $FeCr_2S_4$ polycrystalline sample at different constant external magnetic field, (a) 0.005 T, (b) 0.1 T, (c) 0.5 T, and (d) 1–4.5 T. Insets show enlarged views of the magnetization at low temperatures.

we further investigated the effect of external magnetic field on orbital order. Figure 2 displays the temperature dependence of specific heat in different external magnetic fields for the $FeCr_2S_4$ polycrystalline sample. In agreement with the step-like transition in magnetization, the specific heat displays a well-defined λ-type anomaly around 9 K at zero field, signaling the orbital ordering transition. However, the external magnetic field up to 5 T has no evident influence on the λ-type anomaly, which indicates that the orbital ordering seems to be inert to the changes of magnetic field. Only at ultrahigh fields, e.g., 14 T, the λ-type anomaly shifts to a higher temperature. Being contrary to the inert response to the magnetic field, the orbital ordering is sensitive to the variation of external pressure. See Fig. 3, the onset temperature corresponding to the magnetic anomaly increases with pressure, indicating that the orbital ordering is favored by applying pressure.

As is known, the magnetism might be influenced by the orbital order in more than one way. First, just the orbital degrees of freedom itself, e.g., orbital moment, may contribute to the anomaly of magnetization.[7] Second, the magnetic superexchange interaction is determined by orbital occupation.[12] Third, the magnetic anisotropy is changed due to structure distortion accompanied by the orbital ordering.[13] As shown previously, the magnetization anomaly can be suppressed by applying a magnetic field of 4.5 T, however, a similar magnitude of magnetic field has negligible influence on orbital ordering. Moreover, $FeCr_2S_4$ is a simple Néel-type ferrimagnet at 5 K with antiparallel arrangement between Fe^{2+} and Cr^{3+} spins.[14] Therefore, the former two possibilities could be excluded.

The sensitivity of orbital ordering to the applied external pressure suggests that the orbital ordering seems to rely more on the structure, as the lattice shrinks and the microstructure is modulated by applying pressure. If there is structure distortion below T_{oo} is still in controversy.[14–16] Former powder neutron-scattering revealed that $FeCr_2S_4$ is still cubic down to 4.2 K and single crystal XRD also failed to detect any structure transition across the T_{oo}.[14,15] Nevertheless, recent investigation by high-resolution x-ray synchrotron powder-diffraction showed that the Bragg reflections broaden maximally at T_{oo}, provided clear experimental evidence of a structural anomaly accompanying the orbital ordering transition.[16] As a sequence of reduction of geometrical symmetry, the magnetocrystalline symmetry should be changed, which is related to the domain motion and spin

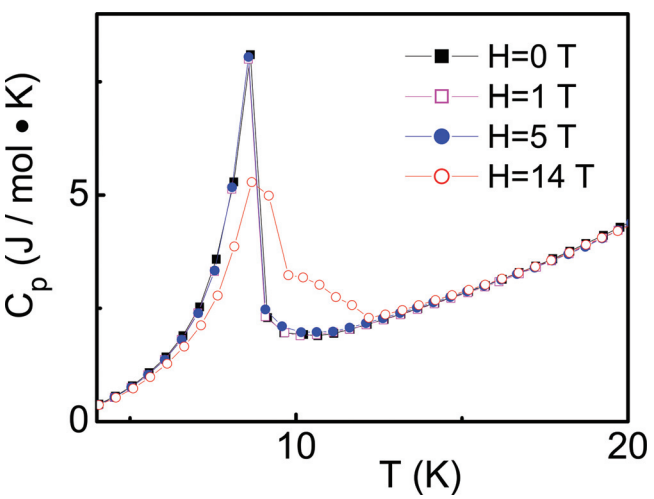

FIG. 2. (Color online) Temperature dependence of the specific heat plotted as C_p vs T at the external magnetic field of $H=0$, 1, 5, and 14 T for the $FeCr_2S_4$ polycrystalline sample.

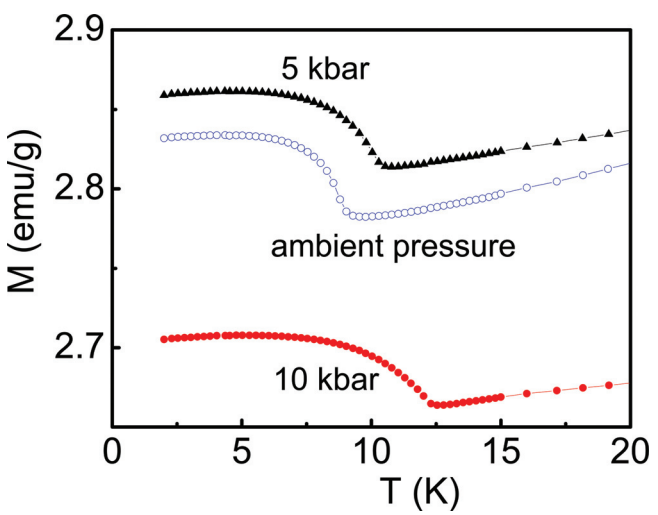

FIG. 3. (Color online) Temperature dependence of FC magnetization at different pressures.

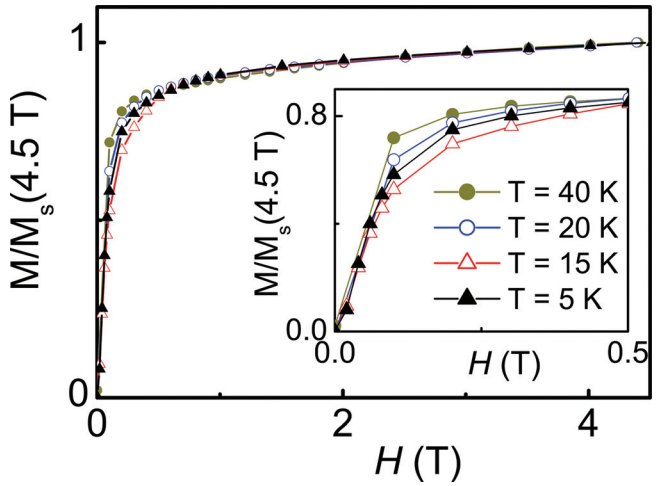

FIG. 4. (Color online) Field dependence of magnetization at 5, 15, 20, and 40 K for the $FeCr_2S_4$ polycrystalline sample. Inset shows enlarged views of the low magnetic field region.

orientation. The investigation on single crystal by magnetic torque revealed that the magnetic anisotropy content increase upon cooling except at lower temperatures around 5 K.[17] However, the experiment is performed on a single crystal sample (with orbital glass and no magnetic anomaly), if it is suitable for a polycrystalline should be examined.

Figure 4 displays the magnetization as a function of field at four different temperatures for a $FeCr_2S_4$ polycrystalline sample. As seen from Fig. 4 and its inset, it is clear that the magnetization reaches saturation harder at 15 K as compared with the magnetizing curves at other temperatures. This indicates that magnetic domains move harder at 15 K and easier at 25 and 5 K, suggesting that the magnetic anisotropy does change nonmonotonously. The nonmonotonous changes of magnetic anisotropy might be caused by the variation of magnetocrystalline symmetry across T_{oo} as discussed earlier.

In a simple Néel-type ferrimagnet, like $FeCr_2S_4$, the domain structure is determined by the collective effect of exchange field, demagnetized factor, external field, and magnetic anisotropy field. The external magnetic field tends to align the magnetic domains in the field direction. The magnetic anisotropy field favors the spins along the easy axis. At low temperature, the value of the anisotropy field varies between 4.3 and 9 T,[18,19] therefore the domain structure at low temperatures and low fields is mainly determined by anisotropy field. With decreasing temperature below T_{oo} at low fields, accompanied by the changes of magnetocrystalline symmetry, the spin in a domain will be reoriented, which contributes to the magnetization anomaly. The orientation of the spins is related by the competition of applied field and anisotropy field. With increasing the external magnetic field, the spin-reorientation effect caused by the changes of magnetocrystalline symmetry will be suppressed gradually.

In summary, the effect of the external magnetic field and pressure on both the magnetic anomaly and orbital ordering transition of polycrystalline $FeCr_2S_4$ has been studied. It is found that the step-like anomaly can be suppressed by applying a magnetic field; however, a similar magnitude of the magnetic field has a negligible influence on orbital ordering. By considering the changes of magnetocrystalline symmetry below T_{oo}, the magnetic anomaly has been explained qualitatively.

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[1]Y. Tokura and N. Nagaosa, Science **288**, 462 (2000).
[2]T. Hotta, Rep. Prog. Phys. **69**, 2061 (2006).
[3]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).
[4]N. Büttgen, J. Hemberger, V. Fritsch, A. Krimmel, M. Mücksch, H.-A. Krug von Nidda, P. Lunkenheimer, R. Fichtl, V. Tsurkan, and A. Loidl, New J. Phys. **6**, 191 (2004).
[5]A. P. Ramirez, R. J. Cava, and J. Krajewski, Nature **386**, 156 (1997).
[6]K. Ohgushi, T. Ogasawara, Y. Okimoto, S. Miyasaka, and Y. Tokura, Phys. Rev. B **72**, 155114 (2005).
[7]V. Tsurkan, V. Fritsch, J. Hemberger, H.-A. Krug von Nidda, D. Samusi, S. Körner, E.-W. Scheidt, S. Horn, R. Tidecks, and A. Loidl, J. Phys. Chem. Solids. **66**, 2036 (2005).
[8]R. Fichtl, P. Lunkenheimer, J. Hemberger, V. Tsurkan, and A. Loidl, J. Non-Cryst. Solids. **351**, 2793 (2005).
[9]S. Shen, Z. R. Yang, R. Tong, G. Li, B. S. Wang, Y. P. Sun, and Y. H. Zhang, J. Magn. Magn. Mater. **321**, 3090 (2009).
[10]Z. R. Yang, S. Tan, and Y. H. Zhang, Appl. Phys. Lett. **79**, 3645 (2001).
[11]R. Tong, Z. R. Yang, S. Shen, X. B. Zhu, Y. P. Sun, L. Li, S. L. Zhang, L. Pi, and Y. H. Zhang, EPL **89**, 57002 (2010).
[12]J. Geck, P. Wochner, S. Kiele1, R. Klingeler, A. Revcolevschi4 M. Zimmermann, B. Büchner, and P. Reutler, New J. Phys. **6**, 152 (2004).
[13]F. Walz, J. Phys: Condens. Matter. **14**, R285–R340 (2002).
[14]G. Shirane, D. E. Cox, and S. J. Pickart, J. Appl. Phys. **33**, 954 (1964).
[15]L. L. Presti, D. Invernizzi, R. Soave, and R. Destro, Chem. Phys. Lett. **416**, 28 (2005).
[16]V. Tsurkan, O. Zaharko, F. Schrettle, Ch. Kant, J. Deisenhofer, H.-A. Krug von Nidda, V. Felea, P. Lemments, J. R. Groza, D. V. Quach, F. Gozzo, and A. Loidl, Phys. Rev. B **81**, 184426 (2010).
[17]K. Ohgushi, Y. Okimoto, T. Ogasawara, S. Miyasaka, and Y. Yokura, J. Phys. Soc. Jpn. **77**, 034713 (2008).
[18]R. P. van Stapele, J. S. van Wieringen, and P. F. Bongers, J. Phys. (Paris). **32**, C1–53 (1971).
[19]L. Goldstein, P. Gibart, and L. Bossard, AIP Conf. Proc. **29**, 405 (1976).