Orbital Freezing and Orbital Glass State in $FeCr_2S_4$

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Low-temperature specific heat measurements and dielectric spectroscopy have been performed on polycrystalline and single-crystalline $FeCr_2S_4$, the single crystals showing a transition into a low-temperature orbital glass phase. The freezing of the orbital moments is revealed by a glasslike specific heat anomaly and by a clear relaxational behavior of the dielectric permittivity, exhibiting several hallmark features of glassy dynamics. The orbital relaxation dynamics continuously slows down over six decades in time, before at the lowest temperatures the glass transition becomes suppressed by quantum tunneling.

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The continuous freezing-in of translational and orientational degrees of freedom into a glass state is a fascinating phenomenon in condensed matter physics and far from being really understood [1]. And despite a long history of research on canonical glass formers, only in recent years has the glassy dynamics been investigated in model systems having perfect long-range translational order but being disordered with respect to the orientational degrees of freedom. Most prominent among those are spin glasses, where disorder and frustrated interactions suppress any long-range magnetic order [2]. Glassy dynamics can also be found in a broad class of materials, including disordered ferroelectrics, diluted molecular crystals, or ortho-para-hydrogen mixtures, which usually are termed orientational glasses (OGs) [3,4]. In OGs, electric dipoles, elastic quadrupoles, or even higher multipolar degrees of freedom cooperatively freeze in devoid of long-range orientational order. Both spin glasses and OGs exhibit a cooperative freezing of diluted moments on a regular lattice into a highly degenerate ground state.

Stimulated by the recent interest in orbital physics and detailed investigations of the orbital liquid (OL) state, one may speculate about yet another class of systems with frozen-in moments, namely, orbital glasses or Jahn-Teller (JT) glasses with a ground state, which is disordered with respect to the orientations of the nonspherical electronic orbitals. The possibility of orbital glass formation has been suggested by Mehran and Stevens [5]. Some experimental hints for the occurrence of orbital glass states have been reported for Sr-doped $LaCoO_3$ [6] and for Cu-doped $LiNH_4SO_4$ [7] and the fact that orbital freezing can be monitored by dielectric spectroscopy has been demonstrated by Babinskii *et al.* [8]. Interestingly, in ferrimagnetic $FeCr_2S_4$ specific heat measurements on slightly off-stoichiometric polycrystalline samples revealed a transition to orbital order (OO) at about 9 K [9]. However, for samples with well-defined stoichiometry, the λ-type anomaly, indicative for a JT-derived structural phase transition, was replaced by a broad hump, reminiscent of the typical anomaly at the glass transition [9]. Thus one might suspect that in $FeCr_2S_4$ OO is indeed easily suppressed and instead an orbital glass state is formed.

A likely mechanism for the formation of an orbital glass state in this material, lacking substitutional disorder, could be the so-called geometric frustration. Geometric frustration was tackled almost 50 years ago by Anderson [10] in treating the magnetism of B-site spinel compounds. It arises, if certain regular but specific arrays of interacting moments cannot satisfy all pairwise interactions [11]. Ising spins on a triangular lattice are an illuminating example. Geometric frustration has been investigated in detail in the spin sector [11], but also should be operative for orbital moments. And indeed, a spin-orbital liquid has been detected recently in $FeSc_2S_4$ [12], revealing that at the A site of cubic normal spinels, spin and orbital moments are geometrically frustrated. Thus, obviously the spinel structure is prone to geometric frustration.

In the present Letter, we provide a thorough specific heat and dielectric investigation of $FeCr_2S_4$ single crystals (SCs) and compare the results to those observed in polycrystals (PCs), which undergo a cooperative JT transition below 10 K. In canonical glass formers, both methods are key techniques for the investigation of the glass transition and glassy dynamics. Especially the exceptionally broad time/frequency window, accessible with dielectric spectroscopy, makes it an ideal tool to follow the many-decade change of molecular kinetics at the glass transition [13]. As in $FeCr_2S_4$ the elastic response of the ionic lattice is coupled to the orbital reorientations via electron-phonon interaction, dielectric spectroscopy also reveals valuable information on the orbital freezing process. In the present letter, we provide clear evidence for an orbital glass state in single-crystalline $FeCr_2S_4$. The slowing down of the mean relaxation time and the distribution of relaxation times are derived in full detail.

PCs of $FeCr_2S_4$ were prepared by solid-state reactions from the high-purity elements. The SCs were grown by a chemical-transport-reaction method with chlorine as the transport agent. The heat capacity was investigated in ^{4}He and ^{3}He/^{4}He-dilution cryostats using adiabatic and relaxational techniques. For the dielectric measurements, silver paint contacts were applied to the platelike samples forming a parallel-plate capacitor. The conductivity and permittivity were measured over a broad frequency range of nine decades ($0.1\ \mathrm{Hz} < \nu < 100\ \mathrm{MHz}$) at temperatures down to 1.4 K. A frequency-response analyzer (Novocontrol α-analyzer) was used for frequencies $\nu < 1$ MHz and a reflectometric technique employing an impedance analyzer (Agilent E 4291A) at $\nu > 1$ MHz [14].

$FeCr_2S_4$ crystallizes in the normal cubic spinel structure [15]. The Cr^{3+} sublattice ($3d^3$, spin $S = 3/2$) is dominated by ferromagnetic exchange. The Fe^{2+} ions ($3d^6$, $S = 2$) are only weakly coupled within the Fe sublattice, but much stronger antiferromagnetically to the Cr ions. Hence $FeCr_2S_4$ reveals ferrimagnetic spin order below $T_c = 170$ K [16]. Fe^{2+} is tetrahedrally coordinated by the sulfur ions; its lower e-doublet is occupied by three electrons and hence is JT active. The octahedrally coordinated Cr^{3+} ions with half filled t_{2g} triplet are not JT active.

Figure 1(a) shows the specific heat C_p/T at low temperatures as measured in polycrystalline and single-crystalline $FeCr_2S_4$. A λ-type anomaly shows up in the PC, signalling long-range OO, which however, seems to be fully suppressed in the SC. In addition, results on the related compound $Fe_{0.5}Cu_{0.5}Cr_2S_4$, which has similar atomic mass and Debye temperature as $FeCr_2S_4$, are included. In this compound the Cu ions are monovalent and all Fe ions have a valence of 3+ ($3d^5$, $S = 5/2$) and hence are not JT active [17]. It is a simple ferrimagnet whose specific heat can be well described by the superposition of a T^3 law for phonons and a $T^{3/2}$ law for magnons, providing a good estimate of the phonon and magnon contributions in $FeCr_2S_4$. The purely orbital contribution to the specific heat of $FeCr_2S_4$, ΔC_p, is obtained by subtracting these contributions, as presented in Fig. 1(b) for the SC. Starting from higher temperatures SC and PC reveal a strong linear contribution to C_p of the order of $\Delta C_p/T \approx 100\ \mathrm{mJ/mol\,K^2}$. It cannot be attributed to an enhanced Sommerfeld coefficient, because $FeCr_2S_4$ is insulating at low temperatures. Therefore, we ascribe it to strongly fluctuating orbitals. Indeed a linear term in the temperature-dependence of the heat capacity was theoretically predicted for OLs [18]. Furthermore, the existence of a dynamic JT effect was originally deduced from Mössbauer experiments [19] and later was termed orbital paramagnetism [20]. These findings support the existence of an orbital liquid state in $FeCr_2S_4$, being characterized by highly cooperative orbital fluctuations.

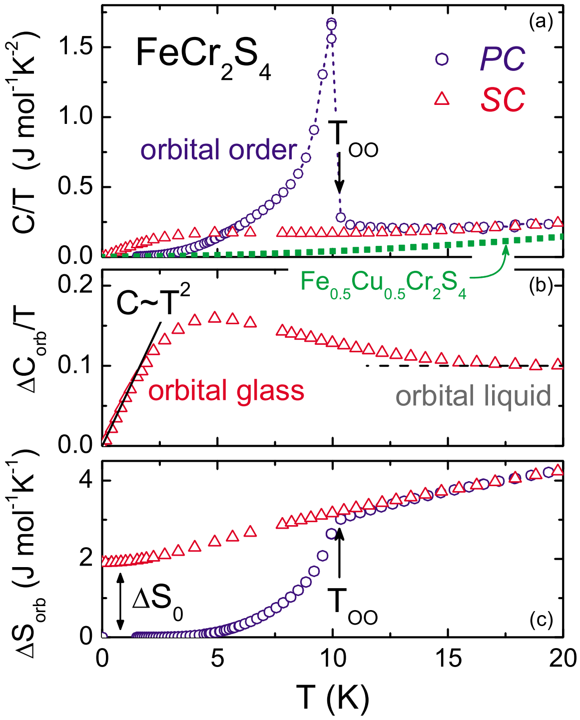

FIG. 1 (color online). (a) Temperature-dependence of the specific heat C_p/T for polycrystalline and single-crystalline $FeCr_2S_4$. The squares indicate C_p/T of $Fe_{0.5}Cu_{0.5}Cr_2S_4$. (b) $\Delta C_p/T$ of single-crystalline $FeCr_2S_4$ arising from the orbital degrees of freedom only (see text). The solid line indicates a $C_p \propto T^2$ dependence. (c) Orbital entropy for the SC and the PC.

At about 10 K, the PC reveals a well-defined λ-type anomaly, which can be ascribed to an OO transition, driven by the JT effect. A magnetic origin can be excluded due to the fully developed ferrimagnetic spin order. However, in the SC, OO is completely suppressed. Instead, its orbital contribution ΔC_p [Fig. 1(b)] exhibits a cusp-shaped maximum, similar to the characteristic behavior of most glass-forming systems close to the glass transition. For low temperatures, C_p approaches zero, following a strict T^2 dependence. In [21], it was shown that random fields can suppress OO and that in systems where OO is absent, the heat capacity follows $C_p \propto T^2$, just as observed here.

Figure 1(c) shows the entropy for the polycrystals and single crystals as obtained by integrating $\Delta C_p(T)/T$ for $0.1 \leq T \leq 20$ K. In the orbitally ordered system, the orbital entropy ΔS_{orb} approaches zero below the OO transition. For the SC a finite entropy for $T \rightarrow 0$ is revealed, clearly demonstrating a macroscopic degeneracy of the ground state, which we interpret in terms of an orbital glass. At $T \rightarrow 0$ K the residual entropy amounts $0.3R\ln 2$, approximately 1/3 of the full entropy of a two-level system. This result surprisingly is quite similar to that observed in spin-ice systems [22]. Even at 20 K the full entropy still has not been reached. Guided by the linear term in the heat capacity above the glass transition, strong orbital fluctuations must still be present, which can be understood in terms of an OL.

Hence, $FeCr_2S_4$ not only belongs to the rare examples of OLs but in addition—depending on the strength of frustration—also reveals transitions into an orbitally ordered or orbital glass state. Guided by the low ordering temperature and by the existence of a well-defined OL, it is clear that geometric frustration has a strong influence on the orbital degrees of freedom. The question, whether the orbital glass state in the SC is driven by geometric frustration and is broken in the PC by marginal disorder or whether long-range OO in the SC is suppressed by slight disorder (e.g., frozen-in strain fields or chlorine defects from the growth process), still remains to be clarified.

Figure 2 shows the conductivity σ' of single-crystalline $FeCr_2S_4$ for various frequencies at temperatures below 20 K. The behavior is dominated by charge transport, namely, a dc contribution, approximately represented by the 0.14 Hz curve, and an ac contribution increasing with frequency, which has a weaker temperature dependence and can be ascribed to hopping transport of localized charge carriers [23]. However, as indicated by the arrows, superimposed to these contributions there is a significant shoulder, indicating an underlying peak that shifts towards lower temperatures with decreasing frequency. Having in mind that $\sigma' \sim \omega\varepsilon''$, this corresponds to a peak in the dielectric loss $\varepsilon''(T)$, too. Thus, Fig. 2 reveals the typical signature of relaxational behavior as commonly observed, e.g., for the glassy freezing of dipolar molecules [3,13]. It is reasonable that the relaxational feature in $\sigma'(T)$, occurring in just the same temperature region as the glasslike hump in the specific heat [Fig. 1(b)], mirrors the glasslike slowing down of orbital dynamics. Further evidence arises from a comparison to the results on the PC sample (inset of Fig. 2), where the orbital degrees of freedom are ordered at low temperatures. As expected, the relaxation feature is absent in the PC, ε'' being more than one decade smaller at the peak temperature of the corresponding SC curve.

In the frequency-dependent plot of Fig. 3, the loss peaks characterizing the orbital relaxation are analyzed in more detail. The solid lines represent fits with the sum of a Cole-Cole (CC) function [24], often employed to describe loss peaks in canonical and OGs, and a conductivity contribution, $\sigma' = \sigma_{dc} + \sigma_0\omega^s$, leading to a divergence of $\varepsilon'' \sim \sigma'/\nu$ towards low ν. The latter is composed of a dc component and an ac power-law contribution with exponent $s < 1$, representing the so-called "universal dielectric response" [25]. For semiconducting systems, the universal dielectric response is the signature of hopping conduction of Anderson-localized charge carriers [23]. Good agreement of fits and experimental spectra could be achieved in this way, the dashed lines showing the relaxational part of the fits. In judging these results one should bear in mind their rather high uncertainty due to a partial correlation of the fit parameters. All the same, as can be deduced even from the raw data, the loss peaks must be broader than for the Debye case, corresponding to a single relaxation time. Thus the relaxation in $FeCr_2S_4$ shows the typical broadening of glassy systems, commonly ascribed to a heterogeneous distribution of relaxation times. With decreasing temperature the loss peak broadens significantly, while its

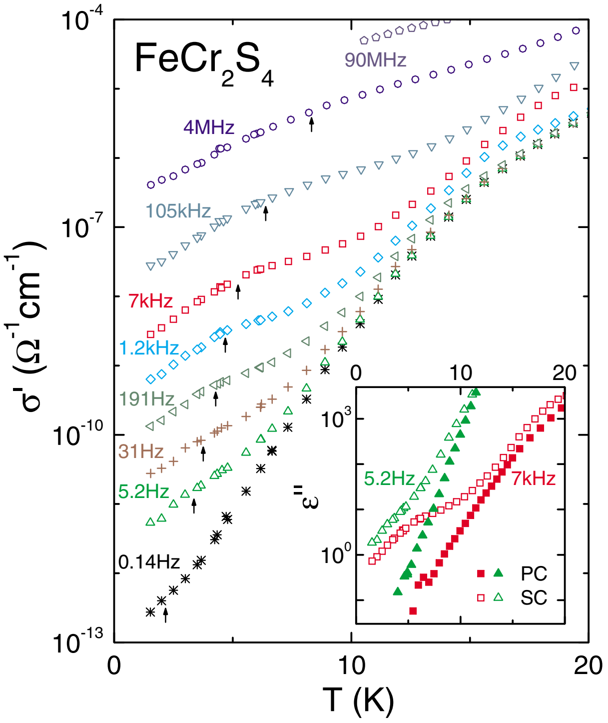

FIG. 2 (color online). Temperature-dependence of the real part of the conductivity in single-crystalline $FeCr_2S_4$ for various frequencies. Inset: Comparison of the dielectric loss in polycrystalline and single-crystalline materials at selected frequencies.

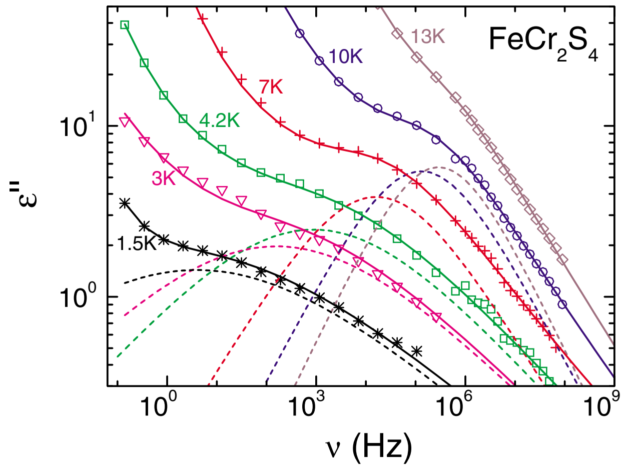

FIG. 3 (color online). Dielectric loss vs frequency at temperatures $T \leq 13$ K. The solid lines represent the results of fits as described in the text. The dashed lines characterize the contributions due to the orbital relaxations.

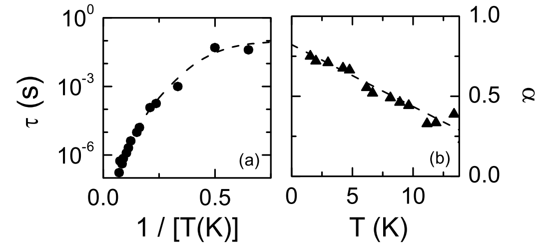

FIG. 4. Temperature dependence of relaxation time (a) and width parameter of the CC distribution (b) as resulting from the fits shown in Fig. 3. The dashed lines are guides to the eyes.

amplitude decreases. Such a behavior of a CC-like loss peak is commonly observed in OGs.

In Fig. 4 the temperature dependencies of the relaxation time τ and the width parameter α are given. The relaxation time, characterizing the reorientational dynamics of the orbitals [Fig. 4(a)], shows a smooth variation over many decades, which is typical for glassy freezing. However, in contrast to most other glassy systems, where the slowing down of the reorientational motion is stronger than an Arrhenius law [1], the temperature dependence of τ becomes weaker for low temperatures. In the Arrhenius representation, $\log(\tau)$ vs $1/T$, a purely thermally activated process corresponds to a straight line, while tunneling would yield a nearly constant $\tau(T)$. Obviously Fig. 4(a) represents a smooth transition from a thermally activated type of reorientation at high temperatures to a purely tunneling type at low temperatures. Thus $\tau(T)$ may never reach the limit of 100 s, where for canonical glass formers the glass transition is often defined. Therefore, strictly spoken, an actual glass state may not be realized in this material. That quantum fluctuations can indeed suppress the glass transition has been demonstrated theoretically for a proton glass [26]. Of course relaxation times in the 0.1–1 s region as observed here at low temperatures certainly are extremely slow for electronic degrees of freedom and can only be understood by taking the intimate coupling of the orbital degrees of freedom to the lattice into account. Figure 4(b) shows the width parameter α of the CC function. $\alpha > 0$ corresponds to symmetrically broadened peaks indicating a distribution of relaxation times, compared to Debye behavior with $\alpha = 0$. α increases linearly with decreasing temperature, which can be understood assuming a temperature-independent Gaussian distribution of energy barriers, leading to loss peaks, whose widths increase like $1/T$ [27].

In conclusion, by specific heat measurements and dielectric spectroscopy, we found experimental evidence for a transition from an OL into an orbital glass state at low temperatures in $FeCr_2S_4$. We find the typical glassy behavior, in particular, a hump in the temperature-dependence of the specific heat, a residual entropy at 0 K, a continuous slowing down of the orbital dynamics, and non-Debye relaxational behavior. Towards 0 K, the heat capacity follows a T^2 dependence, as has been theoretically predicted for a JT glass. From the dielectric results we conclude that there is a Gaussian distribution of hindering barriers against orbital reorientations. In contrast to a conventional glass transition, the complete freezing-in finally is suppressed by quantum-mechanical tunneling, yielding a low-temperature relaxation time of $\tau \simeq 10^{-1}$ s.

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[1] C. A. Angell *et al.*, J. Appl. Phys. **88**, 3113 (2000); D. Ediger, C. A. Angell, and S. R. Nagel, J. Phys. Chem. **100**, 13200 (1996).
[2] K. Binder and A. P. Young, Rev. Mod. Phys. **58**, 801 (1986).
[3] U. T. Höchli, K. Knorr, and A. Loidl, Adv. Phys. **39**, 405 (1990).
[4] K. Binder and J. D. Reger, Adv. Phys. **41**, 547 (1992).
[5] F. Mehran and K. W. H. Stevens, Phys. Rev. B **27**, 2899 (1983).
[6] D. Louca *et al.*, Phys. Rev. B **60**, 10378 (1999).
[7] S. Waplak and W. Bednarski, J. Phys. Condens. Matter **14**, 12529 (2002).
[8] A. V. Babinskii *et al.*, JETP Lett. **57**, 299 (1993).
[9] F. K. Lotgering, A. M. van Diepen, and J. F. Olijhoek, Solid State Commun. **17**, 1149 (1975).
[10] P. W. Anderson, Phys. Rev. **102**, 1008 (1956).
[11] A. P. Ramirez, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier, Amsterdam, 2001), Vol. 13, p. 423.
[12] V. Fritsch *et al.*, Phys. Rev. Lett. **92**, 116401 (2004).
[13] P. Lunkenheimer *et al.*, Contemp. Phys. **41**, 15 (2000).
[14] U. Schneider *et al.*, Ferroelectrics **249**, 89 (2001).
[15] G. Haacke and L. C. Beegle, J. Phys. Chem. Solids **28**, 1699 (1967).
[16] R. P. van Stapele, in *Ferromagnetic Materials*, edited by E. P. Wohlfarth (North Holland Publishing, Amsterdam, 1982) Vol. 3, p. 606.
[17] F. K. Lotgering and R. P. van Stapele, Solid State Commun. **5**, 143 (1967); J. B. Goodenough, J. Phys. Chem. Solids **30**, 261 (1969).
[18] G. Khaliullin and S. Maekawa, Phys. Rev. Lett. **85**, 3950 (2000).
[19] M. R. Spender and A. H. Morrish, Solid State Commun. **11**, 1417 (1972).
[20] L. Brossard *et al.*, Phys. Rev. B **20**, 2933 (1979).
[21] M. A. Ivanov, V. Y. Mitrofanov, L. D. Falkovskaya, and A. Y. Fishman, J. Magn. Magn. Mater. **36**, 26 (1983).
[22] A. P. Ramirez *et al.*, Nature (London) **399**, 333 (1999).
[23] S. R. Elliott, Adv. Phys. **36**, 135 (1987).
[24] K. S. Cole and R. H. Cole, J. Chem. Phys. **9**, 341 (1941).
[25] A. K. Jonscher, Nature (London) **267**, 673 (1977).
[26] V. Dobrosavljević and R. M. Stratt, Phys. Rev. B **36**, 8484 (1987).
[27] N. Birge *et al.*, Phys. Rev. B **30**, 2306 (1984).