Orbital fluctuations and orbital order in $FeCr_2S_4$

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1. Introduction

Orbital physics has become an important topic in modern solid-state physics and materials science. In transition-metal oxides the shape and anisotropy of the electron density of the d-electrons determine the fundamental electronic properties. The sensitivity of the magnetic exchange to the spatial orientation of the orbitals governs the long-range order of the spin degrees of freedom. If the orientational order of the orbitals can be changed by an external field (strain field, optical excitation or electric field), the magnetic order will be changed concomitantly. The possibility to tune electronic orbitals by external fields has been recently proposed as essential ingredient of a future correlated-electron technology [1].

The strong coupling of spin, charge, and orbital degrees of freedom yields complex and fascinating ground states. Electron-phonon coupling usually lifts the orbital degeneracy and results in a long-range orbital order and in a change of the crystal symmetry via the Jahn–Teller (JT) effect [2]. In Mott–Hubbard insulators orbital order can also be established via the Kugel–Khomskii mechanism [3] when the orbital degeneracy is lifted by purely electronic interactions. However, recently it has been suggested that the exchange in orbitally degenerate systems is strongly frustrated and even in cubic lattices the orbitals may remain disordered down to 0 K, forming an orbital liquid [4–7]. The appropriate candidates for orbital liquids are Mott–Hubbard insulators with electrons with threefold degeneracy in octahedral or twofold degeneracy in tetrahedral crystal fields [8] and where, in addition, the electronic orbitals are coupled via strongly frustrated exchange interactions induced by disorder or geometric frustration. Frustration results in a dynamic liquid ground state or in a glassy freezing of the internal degrees of freedom at low temperatures. Regarding spin systems frustration in structurally disordered magnets yields a spin-glass state [9], and in geometrically frustrated [10] compounds results in spin-liquid [11] or spin-ice [12,13] states. Frustration effects on the orbital degrees of freedom have been much less examined. Reports on orbital liquids or orbital glasses are rare [14–16], although orbital ordering has been observed in a variety of d-electron systems.

Here we provide experimental evidence for an orbital liquid and an orbital glass state in a ferrimagnet with perfect spin order. We focus on the orbital degrees of freedom of the magnetic semiconductor compound $FeCr_2S_4$, which recently attracted considerable attention due to its colossal magnetoresistance effect [17]. It crystallizes in a normal spinel structure AB_2S_4. The Cr^{3+} sublattice (electronic configuration $3d^3$, spin $S=3/2$) is dominated by ferromagnetic exchange. The Fe^{2+} ions ($3d^6$, $S=2$) are only weakly antiferromagnetically coupled within the sublattice, but much stronger antiferromagnetically to the Cr ions resulting in ferrimagnetic spin order with the Fe^{2+} and Cr^{3+} magnetic moments aligned antiparallel to each

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other. Concerning the orbital degrees of freedom, the orbital moment of the Cr^{3+} ion is quenched. The lower orbitally degenerated *e*-doublet of Fe^{2+} is JT active and, thus, determines the orbital properties of $FeCr_2S_4$.

2. Experimental

$FeCr_2S_4$ polycrystals (PC) were prepared by solid-state reactions. The single crystals (SC) were grown by a chemical-transport-reaction method with chlorine as the transport agent. The composition and phase homogeneity of the samples were checked by electron-probe microanalysis and X-ray diffraction. The microanalysis revealed a nearly perfect Fe/Cr and cation/anion ratio for the samples. About 1% of chlorine ions were also detected in the single crystal. The sample stoichiometry of the polycrystals was tuned by heat treatment in vacuum and sulphur atmosphere. The magnetization was measured by a commercial SQUID magnetometer MPMS-7 (Quantum Design). The heat capacity was measured for different magnetic fields up to 100 kOe in ^{4}He cryostats using adiabatic and relaxation techniques for temperatures $2 < T < 50$ K and in a ^{3}He/^{4}He dilution refrigerator using relaxation technique for temperatures $0.05 < T < 2.5$ K.

3. Results and discussion

Fig. 1 shows the temperature dependence of the magnetization $M(T)$ for the single and polycrystalline as-grown samples at low fields. At $T_C = 167$ K a step-like anomaly in $M(T)$ reveals the onset of ferrimagnetic order. In the single crystal a cusp at 60 K and splitting of the field cooled (FC) and zero-field cooled (ZFC) curves indicate domain-reorientation processes [18]. In the polycrystal the ZFC and FC curves split already at the Curie temperature due to pinning of the magnetic domain walls by grain boundaries. Below the cusp-like anomaly both, the poly- and the single crystals exhibit a pronounced downturn in the ZFC magnetization. However, only the polycrystal shows a clear step-like decrease (increase) in the ZFC (FC) magnetization, respectively, at $T_{OO} \approx 10$ K. This transition temperature we ascribe to the orbital ordering temperature T_{OO}. The accompanying magnetic anomaly at T_{OO} coincides with the low-temperature transition detected earlier by specific-heat and Mössbauer experiments in polycrystalline samples [19–21] associated with a JT-like transition resulting in a long-range orbital order. The measured saturation magnetization M_S of the single crystal of about 1.88 μ_B is consistent with the ferrimagnetic order of Cr with $M_S(2Cr^{3+}) = 6\ \mu_B$/f.u. and Fe with $M_S(Fe^{2+}) = 4.12\ \mu_B$/f.u., taking into account the enhanced *g*-value of Fe^{2+} ($g \approx 2.06$) due to spin-orbit coupling. Thus, a fully developed spin order at temperatures below 167 K is established, as already shown by neutron-scattering studies [22]. This suggests that the low-temperature anomalies are governed by the orbital degrees of freedom, only.

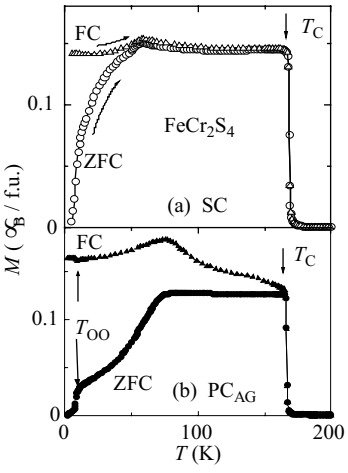

Fig. 1. Temperature dependence of the zero-field cooled (ZFC) and field cooled (FC) magnetization in a field of 100 Oe for an as-grown $FeCr_2S_4$ single crystal (a), and in a field of 50 Oe for an as-grown polycrystal (b). The arrows at T_C and T_{OO} indicate the Curie temperature and orbital ordering temperature, respectively.

Fig. 2 compares the specific heat at low temperatures and at different magnetic fields in the representation C_p/T vs T as measured in the as-grown polycrystal (Fig. 2a) as well as in the single crystal (Fig. 2b). The polycrystal reveals the well-defined λ-type anomaly of the transition into orbital order reported earlier [20]. In the single crystal, however, the transition is completely suppressed. Instead, the specific heat passes through a cusp-shaped maximum and goes to zero following a strict T^2-dependence. Such a quadratic low-temperature law has been theoretically predicted for an orbital glass formed in a lattice of Jahn–Teller ions under the influence of random fields [14]. Note that in canonical spin glasses also a cusp-like maximum is observed above the freezing temperature, but a linear term evolves towards zero temperature [9] in contrast to the present T^2-dependence. The orbital character of the glassy ground state in $FeCr_2S_4$ single crystals is further supported by ac-susceptibility measurements, which definitely ruled out a spin-glass state [18].

Another important hint on the orbital origin of the low-temperature transitions in $FeCr_2S_4$ is given by the effect of an external magnetic field on the specific heat. Fig. 2a shows that

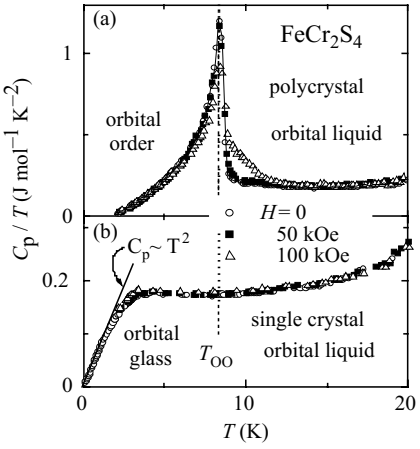

Fig. 2. Temperature dependence of the specific heat as C_p/T vs T at different magnetic fields: a) for the as-grown polycrystal, b) for the as-grown single crystal.

the magnitude of the λ-anomaly in the polycrystal becomes slightly reduced, but without any noticeable shift of the ordering temperature. Only at a field of 100 kOe a weak increase of the specific heat becomes apparent just above T_{OO}. If the λ-anomaly was related to a transition in the spin system, a much stronger influence of the magnetic field has to be expected, as, e.g. observed in $MnCr_2S_4$, where the competing magnetic interactions of the Mn and Cr sublattice give rise to a second magnetic transition from the collinear ferrimagnetic phase into a triangular structure [23]. Therefore, the λ-anomaly in the specific heat in $FeCr_2S_4$ has to be attributed to the onset of orbital order. The same holds for the glassy freezing in the single crystal, as one can see in Fig. 2b, where the specific heat data measured in different magnetic fields essentially coincide with each other.

Above the T_{OO} both polycrystal and single crystal reveal a comparably large specific heat, which can neither be explained by a T^3 phonon nor a $T^{3/2}$ magnon contribution. But its extrapolation to zero temperature rather suggests a highly enhanced linear contribution to the specific heat C_p of the order of $\Delta C_p/T \approx 100$ mJ mol^{-1} K^{-2}. This linear contribution cannot be attributed to an enhanced Sommerfeld coefficient, because $FeCr_2S_4$ is insulating at low temperatures [17,24]. Therefore, we ascribe it to the strongly fluctuating orbitals. It is worth to note that a linear term in the temperature dependence of the heat capacity has been recently predicted for an orbital liquid [25]. Furthermore, the existence of a dynamic JT effect has been originally deduced from Mössbauer experiments [19] and later on has been termed as orbital paramagnetism [21]. The dynamic JT effect as well as orbital paramagnetism indicate orbital fluctuations and provide an orbital liquid state.

The specific heat data of $FeCr_2S_4$ presented in Fig. 2 reveal the scenario of an orbital liquid state within a fully ordered spin system. Like in $FeSc_2S_4$ the orbital liquid state is most probably a consequence of the geometric frustration of the *A*-site in the spinel structure [26]. But whereas in the single crystal the orbitals remain disordered down to lowest temperatures investigated, they finally order in the polycrystal. Several reasons can be responsible for this different behavior. The interplay of disorder induced by anion and cation defects, charge balance, lattice strain and magnetic anisotropy has to be taken into account. The small amount of chlorine ions in the single crystal may be important for suppression of the orbital order like in $LaMnO_3$, where small changes of the oxygen content are enough to disturb the charge balance and to destroy the cooperative Jahn–Teller effect [27]. The effect of non-stoichiometry in $FeCr_2S_4$ is illustrated in Fig. 3, which compares the temperature dependence of the heat capacity as C_p/T vs T for three polycrystals after different heat treatment. Vacuum annealing increases the phase-transition temperature into orbital order with respect to the as-grown sample, whereas sulphur annealing strongly decreases and broadens the transition. This indicates the high sensitivity of the ground state to the stoichiometry. But more detailed experiments are necessary to draw a final conclusion on the mechanism of formation of the orbital glass.

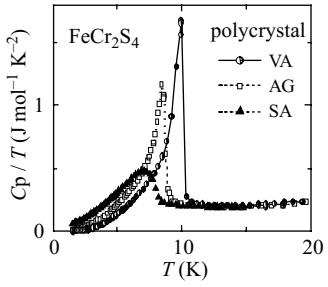

Fig. 3. Temperature dependence of the specific heat as C_p/T vs T for as-grown (AG), vacuum annealed (VA) and sulphur annealed (SA) polycrystalline samples.

4. Summary

The specific heat of $FeCr_2S_4$ poly- and single crystals was studied for temperatures $0.1 \leq T \leq 30$ K in magnetic fields up to 100 kOe. Concomitant anomalies of the specific heat and the low-field magnetization were found at temperatures below 10 K, which are strongly influenced by heat treatment of the samples in vacuum or sulphur atmosphere. The specific heat of the polycrystalline samples exhibits a λ-type anomaly at around 10 K, while in the single crystals a broad maximum in the specific heat at around 5 K replaces the λ-anomaly, followed by a strict T^2-dependence in the temperature range $0.1 \leq T \leq 2$ K. For temperatures from 5 to 20 K a linear term was found in the specific heat with a high value of $\Delta C_p/T \approx 100$ mJ mol^{-1} K^{-2}, both for poly- and single crystals. Magnetic field has no sizable influence on the specific heat. These results suggest the formation of an orbital liquid state above 10 K both for poly- and single crystals, orbital ordering at 10 K in polycrystals and an orbital glass state below 5 K in single crystals. Thus, our results provide clear experimental evidence of an orbital liquid to orbital glass transition in a 3d-magnetic system.

Acknowledgements

The support of the BMBF via VDI/EKM, FKZ 13N6917/18 and by DFG within SFB 484 (Augsburg) and US CRDF-MRDA via grant MP2-3047 (Chisinau) is gratefully acknowledged.

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