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Spin-Glass State in Defect-Fluorite $Er_2Zr_2O_7$

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Low-temperature magnetic properties of $Er_2Zr_2O_7$ were studied by magnetization measurements on a newly prepared single crystal. Simultaneously, powder neutron diffraction was employed to investigate its microscopic properties down to 0.3 K. Our low-temperature data demonstrate the presence of a magnetic signal (short-range correlations) by (i) bifurcation of zero-field-cooled (ZFC) and field-cooled (FC) data, and (ii) diffuse magnetic scattering signal developing well in agreement with the temperature development of bulk properties. The presented data are discussed in the frame of a spin-glass ground state in $Er_2Zr_2O_7$.

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1. Introduction

The rare-earth oxides of the general formula $A_2B_2O_7$, with A being a rare-earth ion and B a d- or p-metal, have been extensively studied for their frequently exotic electronic properties. The majority of the $A_2B_2O_7$ oxides crystallize in a cubic structure of pyrochlore-type (space-group Fd-3m, 227) or defect-fluorite-type (space-group Fm-3m, 225). The former structure with both A and B sites, separately, forming lattices of corner sharing tetrahedra, represents a canonical example of a frustrated lattice. When magnetic ions reside on the A or B sites, the formation of long-range ordered magnetic ground-states is suppressed due to competing exchange interactions. This suppression can lead to the formation of strongly-correlated unconventional ground-states. The pyrochlore oxides have been found to host a wide range of exotic states ranging from spin-glasses, to spin-liquid and spin-ices [1], with spin-ices capable of hosting magnetic and electric monopole-like excitations [2]. The defect-fluorite structure is another example of a geometrically frustrated lattice. However, a limited number of low-T studies on $A_2B_2O_7$ oxides crystallizing in this structure has been reported.

The structural properties (as well as electronic properties) of rare-earth $A_2B_2O_7$ oxides are strongly dependent on the size of ratio between A and B cations (r_A/r_B). Focusing on the $A_2Zr_2O_7$, the content of present study, all so-far investigated rare-earth zirconates crystallize in a cubic pyrochlore structure at room temperature and pressure when $1.46 \leq r_A/r_{Zr} \leq 1.78$, i.e., A = La–Gd. On heating an order-disorder transition to a defect fluorite structure is observed for A = Nd–Gd [3]. Alternatively, applied pressure induces a transition to a lower symmetry structure (space-group $Pnma$, 62) [4]. For A being a heavy rare-earth the size difference between ions is reduced leading to significant thermodynamic drive for A/B mixing. When $r_A/r_{Zr} < 1.45$ the pyrochlore structure-type becomes unstable. Disorder of A/Zr and anion occupancy randomisation result in a defect-fluorite (long-range) structure.

$A_2Zr_2O_7$ adopting a pyrochlore lattice have been studied in detail (a number of papers, e.g. [5–8] and references therein). Zirconates with A being a heavy rare-earth element have been investigated almost exclusively from the viewpoint of structure stability under extreme conditions being suitable materials for photochemical catalyst [9], magneto-hydrodynamic power generation [10], or storage of nuclear waste [11–13]. A systemic study, especially in low-temperature region, is missing.

Our very recent measurements [14] on a single crystal allowed us to confirm $Er_2Zr_2O_7$ crystalizing in (long-range) defect-fluorite structure. The magnetization measurements exhibit Curie-Weiss (C-W) behaviour down to $T < 50$ K, with a fitted C-W temperature −13.2(2) K, and the effective magnetic moment close to that of an Er^{3+} free ion (9.55 μ_B/Er^{3+}). No pronounced anisotropy was observed in the measurements down to 5 K. At low temperatures, a weak feature in M/H vs. T (and bifurcation of zero-field-cooled (ZFC) and field-cooled (FC) data) is seen for external magnetic fields < 0.1 T applied along (111) crystallographic direction. Higher fields broaden and shift the feature to higher temperatures. Specific heat shows an accompanying broad anomaly with a similar field dependence. Together with a frequency dependence of ac-susceptibility, our data suggest a spin-glass transition at ∼ 0.6 K in $Er_2Zr_2O_7$.

The present paper follows our recent study on an $Er_2Zr_2O_7$ single crystal [14]. We are presenting both so far not published low-temperature data on the single crystal and our first neutron diffraction data on a powder sample. The obtained results are dominated by a pronounced low-temperature anomaly of magnetic

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origin in all types of measurements. Measured diffraction patterns contained except nuclear (reflections) peaks also a magnetic feature at around 1.1 $Å^{-1}$. The temperature evolution of the magnetic signal is well in agreement with a development of the low-temperature anomaly observed in our single crystal data.

2. Results and discussion

An $Er_2Zr_2O_7$ single crystal was prepared for the first time, being concurrently the first single crystal in $A_2Zr_2O_7$ family adopting the defect-fluorite type of cubic structure [14, 15]. The sample quality and homogeneity were checked by means of X-ray and neutron diffraction and energy dispersive analysis. Magnetization measurements were conducted on prism-shaped samples cut from the prepared ingot with the long axes parallel to crystallographic directions [100], [110], and [111], respectively. The low-temperature (down to 0.4 K) magnetization data were obtained measuring electrical resistivity of pre-calibrated Hall probes (Arepoc Company) attached to the sample and Physical Property Measurement System (PPMS, Quantum Design) [16, 17]. Absolute values of magnetization were obtained by scaling the Hall probe data to data measured at higher temperatures using Magnetic Property Measurement System (MPMS, Quantum Design).

Magnetization data $M/H(T)$ shown in Fig. 1 were measured under both zero-field-cooled (ZFC) and field-cooled (FC) regimes in an external magnetic field applied along principal crystallographic directions, namely [111], [110], and [100]. A bifurcation of ZFC and FC data is observed below 2.5 K in applied magnetic field of 0.05 T along all three crystallographic directions. Negligible difference between ZFC and FC data is followed in higher field ($\geq$ 0.10 T), see Fig. 1. The magnetization increases with decreasing temperature almost linearly down to 2.5 K and changes its slope at lower temperatures. It is well demonstrated on a temperature evolution of the minimum in the first derivative of magnetization data (Fig. 1). A pronounced minimum in derivative is located at around 0.8 K for all three crystallographic directions. In fact, this result is in good agreement with specific heat and ac-susceptibility data anomalies presented in [14]. The low-temperature data measured on an $Er_2Zr_2O_7$ single crystal are clearly not consistent with paramagnetic ground state. Together with results of neutron diffraction experiment (below) suggest the presence of short-range correlations at low temperature.

A neutron diffraction experiment was performed on powdered $Er_2Zr_2O_7$ single crystal (of 4 g mass) employing focusing powder diffractometer E6 in Helmholz Zentrum Berlin (HZB). The neutron wavelength of 2.436 Å was used. To attain temperatures as low as 0.3 K and a good thermal coupling between powder grains at lowest temperatures, (i) LT-HS-2 Sorption pumped ^{3}He cryostat was provided by HZB, and (ii) the sample was inserted into copper container together with a mixture of deuterated ethanol and methanol. We note that ethanol-methanol mixture contribute to the diffraction patterns by a broad anomaly at around 1.8 $Å^{-1}$. The diffraction patterns are further contaminated by peaks originating from diffraction of the Cu sample container and the Al walls of the cryostat. None of these peaks coincide with $Er_2Zr_2O_7$ nuclear reflections.

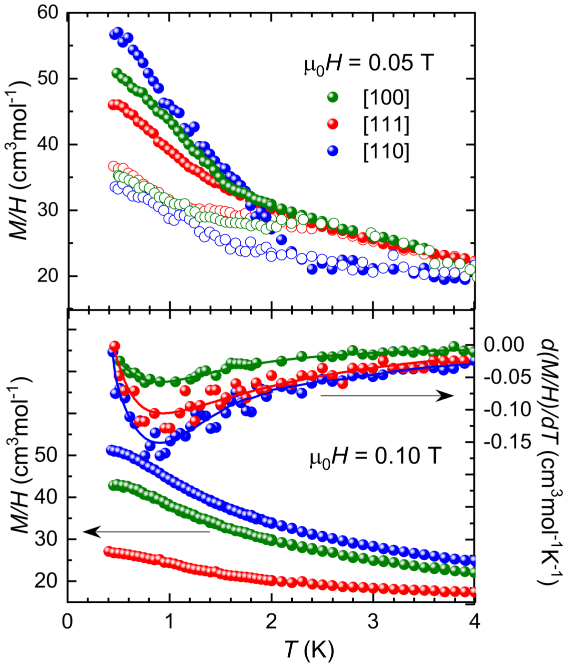

Fig. 1. Temperature dependence of magnetization in low-temperature region. External magnetic field was applied along principal crystallographic directions. First derivatives of magnetization data measured in 0.10 T are shown as well.

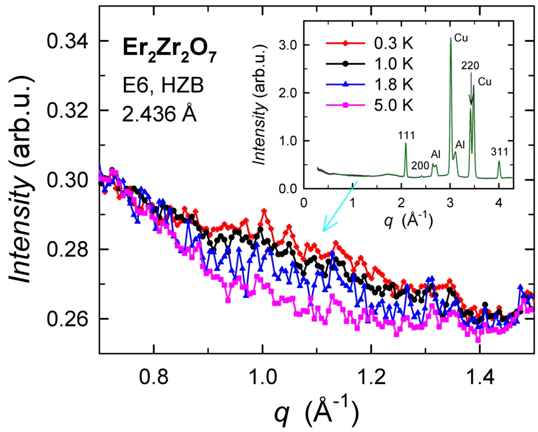

Fig. 2. Neutron diffraction patterns measured on powder $Er_2Zr_2O_7$. The temperature evolution of magnetic signal at around 1.1 $Å^{-1}$ is followed. Inset contains whole measured diffraction patterns. Individual nuclear reflections are marked together with sample environment Cu and Al peaks.

The neutron diffraction experiment confirmed the sample homogeneity and phase purity within the whole sample volume. The measured diffraction patterns contain, besides nuclear (reflections) peaks, a broad magnetic feature at $q \approx 1.1$ Å^{-1} (Fig. 2). The intensity of this feature decreases with increasing temperature from 0.3 K to 5.0 K and remains the same (zero with respect to the experimental background) at higher temperature. The temperature evolution of the magnetic signal is well in agreement with the development of the magnetization anomaly (Fig. 1) and specific heat data [14]. The anomaly in specific heat and bifurcation of ZFC and FC magnetization data are found well below 5 K.

The observed magnetic feature in diffraction patterns can be ascribed to diffuse scattering signal originating from short-range magnetic correlations between Er cations, and it strongly supports our assumptions of spin-glass ground state in $Er_2Zr_2O_7$ [14]. Further experiments to unambiguously characterize the ground state of $Er_2Zr_2O_7$, e.g. our recent polarized neutron scattering experiment down to low temperatures (D7, ILL), are highly desirable.

3. Conclusions

Magnetic properties of $Er_2Zr_2O_7$ were studied down to low temperature (0.3 K) employing magnetization and powder neutron diffraction measurements. The bifurcation of ZFC and FC data, a weak feature in $M(T)$ shifted to higher temperatures with applied magnetic field and diffuse magnetic signal developing with temperature documented a presence of magnetic short-range correlations in the compound. Obtained data were discussed in the frame of a spin-glass ground state in $Er_2Zr_2O_7$.

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