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Heat capacity of rare-earth aluminum garnets

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ABSTRACT

Heat capacity of the single crystalline $Er_xY_{3-x}Al_5O_{12}$ (x = 0, 0.6, 1.1, 3), $Er_2HoAl_5O_{12}$, and $Ho_{1.5}Y_{1.5}Al_5O_{12}$ garnets was measured in the temperature range from 1.9 to 220 K at zero magnetic field and at fields up to 9 T. The Schottky anomalies were found for the garnets with magnetic ions. The heat capacity was fitted by a sum of the Debye, Einstein, and Schottky contributions. The entropy and magnetic entropy were evaluated. The magnetic entropy magnitude in the garnets with erbium ions suggests the application of these garnets in adiabatic demagnetization refrigerators.

1. Introduction

Rare-earth aluminum garnets, $Re_3Al_5O_{12}$ (Re —rare-earth elements), are the most common laser crystalline materials [1,2]. The aluminum garnets, primarily the aluminum yttrium garnet, have also important applications in high-temperature ceramic composites due to their excellent creep-resistance [3]. At present, the $Re_3Al_5O_{12}$ garnets are widely discussed as promising materials for other numerous practical applications. It was suggested in Ref. [4] to use some $Re_3Al_5O_{12}$ in adiabatic demagnetization refrigerators. This stimulated additional interest in caloric properties of rare-earth aluminum garnets, especially in the impact of magnetic field on their heat capacity. There is a surprising lack of information on thermodynamic properties of the aluminum garnets at low temperature and on the influence of magnetic field on them. For the $Ho_3Al_5O_{12}$ single crystal the heat capacity was measured only at zero magnetic field below 20 K [5]. The observed results were treated taking into account the Debye and Schottky contributions and the influence of the antiferromagnetic phase transition with admixture of quadrupole effects. For the pure nonmagnetic $Y_3Al_5O_{12}$ garnet the temperature variation of the heat capacity was observed from low temperatures up to 900 K in Ref. [6] and for the pure yttrium garnet and $Y_3Al_5O_{12}$ slightly doped with Nd at high temperatures above 300 K in Ref. [7]. The temperature dependences of the heat capacity in Ref. [7] were fitted using a polynomial function. The heat capacity of a $Y_3Al_5O_{12}$ crystal with 30% of Er ions substituted for Y was obtained in Ref. [4] within a range from 93 mK up to 8 K at zero magnetic field and fields up to 8 T. A hump found at zero magnetic field near 266 mK was ascribed to the splitting of the ground Kramers doublet by local magnetic fields induced by neighbors while the broad maxima emerged at external fields were explained as Schottky-like anomalies due to removing the Kramers degeneration. Sharp steps in the low-temperature heat capacity at strong magnetic fields were observed for an erbium-holmium mixed garnet in Ref. [8].

In the present paper we report measurements of the heat capacity in several pure and mixed rare-earth aluminum garnets within a temperature range from 1.9 to 220 K at magnetic fields up to 9 T. The caloric properties for the garnets under study, except for the aluminum yttrium garnet, were not previously reported as far as we know.

2. Samples and experiment

The pure and mixed $Er_xY_{3-x}Al_5O_{12}$ (x = 0, 0.6, 1.1, 3), $Er_2HoAl_5O_{12}$, and $Ho_{1.5}Y_{1.5}Al_5O_{12}$ garnet single crystals were grown by the horizontal Bridgman directional solidification method in a molybdenum crucible. The densities of the garnets are listed in

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Table 1. To get samples for heat capacity measurements, plates with faces perpendicular to the crystal cubic axis were cut from the ingots. The plate thickness was near 0.3 mm and the face area was near 0.2 cm^2.

In the aluminum garnets the rare-earth trivalent Y^{3+}, Er^{3+}, and Ho^{3+} ions occupy the dodecahedral c-sites of the crystalline lattice. The formula unit comprises 20 ions. The garnets have the $Ia\bar{3}d$ space symmetry. The c-sites are in the vertices of two interpenetrating triangular sublattices and form a hyperkagome structure [9].

The heat capacity was measured with a Quantum Design Physical Property Measurement Systems PPMS-9 + Ever-Cool-II using the built-in conventional procedure. Measurements were carried out within the temperature ranges 1.9 to 220 K in magnetic fields from 0 to 9 T.

3. Results

The heat capacity data obtained for the crystals of the $Er_xY_{3-x}Al_5O_{12}$ set in zero magnetic field are shown in Fig. 1. The heat capacity data for the $Er_2HoAl_5O_{12}$ and $Ho_{1.5}Y_{1.5}Al_5O_{12}$ single crystals in zero magnetic field are shown in Fig. 2. The insets to these figures demonstrate the heat capacity below 35 K to make more visible the low-temperature anomalies. The heat capacity at low temperatures for the samples comprising the Er^{3+} and Ho^{3+} ions is dominated by the Schottky anomalies [4,10] as in various other insulator crystals with magnetic ions [11,12]. At higher temperature the lattice (phonon) contribution prevails [10,11]. For the yttrium aluminum garnet the Schottky contribution does not exist, the heat capacity is entirely determined by the phonon contribution.

The application of the magnetic field does not affect the heat capacity in the yttrium aluminum garnet as the lattice contribution is insensitive towards magnetic field (not shown). The application of magnetic field to other garnets under study influences remarkably the heat capacity at low temperatures. Figs. 3–5 show the temperature dependences of the heat capacity in magnetic field for the $Er_{1.1}Y_{1.9}Al_5O_{12}$, $Er_2HoAl_5O_{12}$, and $Ho_{1.5}Y_{1.5}Al_5O_{12}$ garnets below 40 K, respectively.

4. Discussion

The heat capacity in insulator crystals with magnetic ions can be caused by several independent contributions: phonon contribution, Schottky anomalies, and anomalies due to phase transitions [10]. The aluminum garnet crystals do not show structural phase transitions up to their melting [2]. Magnetic ordering in the garnets is affected by crystalline symmetry. The rare-earth magnetic moments at the dodecahedral c-sites are in the vertices of two interpenetrating triangular sublattices and form a hyperkagome structure [9]. In such a structure the magnetic moments cannot be antiparallel pairwise. This leads to geometric frustration and may give rise to exotic response to the applied strong magnetic field as it was observed, for instance, in the $Tb_3Ga_5O_{12}$ [9] and $Er_2HoAl_5O_{12}$ [13] garnets. In addition, the crystalline structure of garnets reduces remarkably the magnetic phase transition temperatures. The antiferromagnetic phase transitions were observed in the $Er_3Al_5O_{12}$ and $Ho_3Al_5O_{12}$ garnets at temperatures 0.054 and 0.839 K, respectively [5,14]. In the mixed erbium-yttrium garnets the Neel temperature was found to decrease compared to $Er_3Al_5O_{12}$ with decreasing erbium concentration [14]. Therefore, the antiferromagnetic phase transitions in the $Er_{1.1}Y_{1.9}Al_5O_{12}$ and $Er_{0.6}Y_{2.4}Al_5O_{12}$

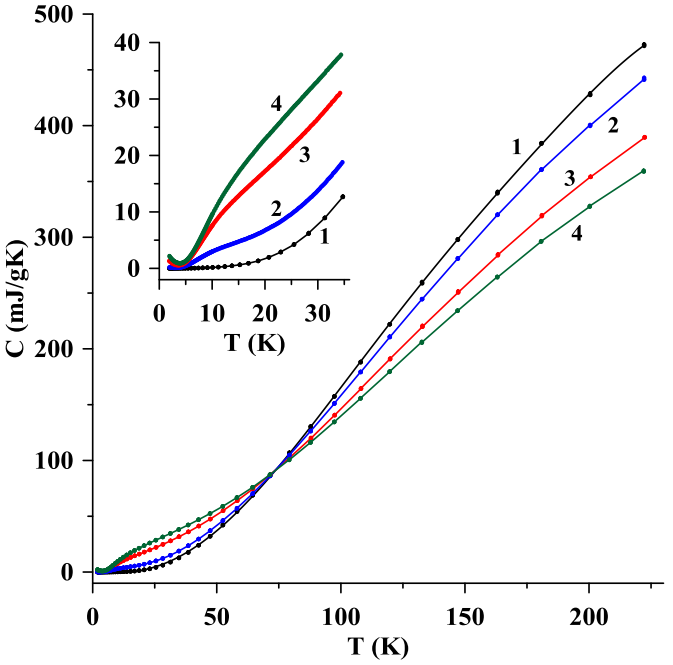

Fig. 1. Temperature dependences of heat capacity for the $Er_xY_{3-x}Al_5O_{12}$ set in zero magnetic field. The numbers from 1 to 4 in the panel correspond to x equal to 0, 0.6, 1.1, and 3, respectively. The inset shows the heat capacity below 35 K.

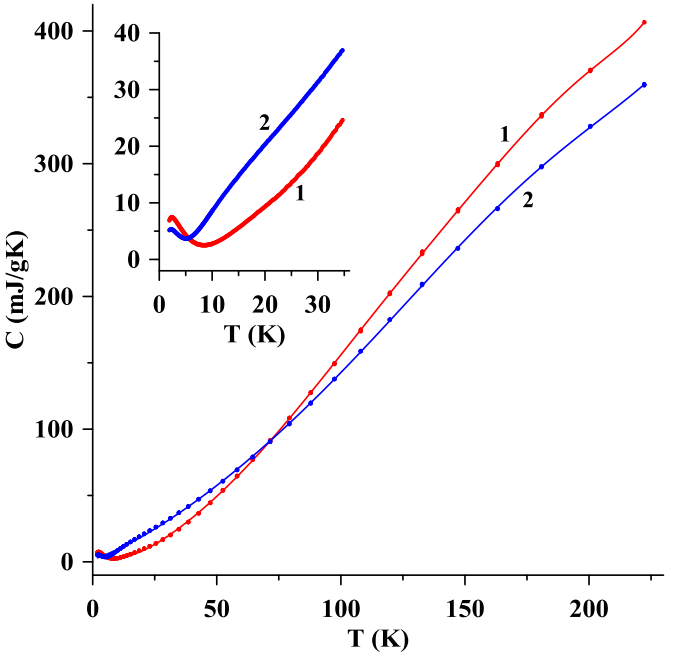

Fig. 2. Temperature dependences of heat capacity for the $Ho_{1.5}Y_{1.5}Al_5O_{12}$ (1) and $Er_2HoAl_5O_{12}$ (2) single crystals in zero magnetic field. The inset shows the heat capacity below 35 K.

Table 1
Densities of the garnets under study in g/cm^3.

$Y_3Al_5O_{12}$	$Er_3Al_5O_{12}$	$Er_{0.6}Y_{2.4}Al_5O_{12}$	$Er_{1.1}Y_{1.9}Al_5O_{12}$	$Er_2HoAl_5O_{12}$	$Ho_{1.5}Y_{1.5}Al_5O_{12}$
4.553	6.397	4.964	5.230	6.336	5.431