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Thermal and magnetic properties of regenerator material Gd_2O_2S

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Abstract. Magnetic materials play a significant role in improvement of regenerative cryocooler performance, because they have high volumetric specific heat at magnetic transition temperatures. Gadolinium oxysulfide (Gd_2O_2S, GOS) that has an antiferromagnetic transition at 5 K improved the cooling performance of cryocoolers when it was used in colder side of the second stage regenerator operating below 10 K. Small magnetic susceptibility and specific heat insensitive to magnetic field is important in order to reduce influence of magnetic field on the performance of cryocooler. We measured magnetization and specific heat of ceramic GOS in magnetic field up to 5 T. The magnetization of GOS represented typical temperature dependence for antiferromagnetic materials and no metamagnetic transition was observed. As for specific heat of GOS, peak temperature decreased from 5.5 to 5.0 K with increasing magnetic field from 0 to 5 T and the transitions remained sharp in magnetic fields. Thermal conductivity of GOS was observed to have very small magnetic field dependence.

1. Introduction

Cryocoolers with lowest temperature of 4 K realized superconducting magnet systems and ^{3}He-^{4}He dilution refrigerators without liquid helium. In order to improve regenerative cryocooler performance, magnetic materials play a significant role in regenerator efficiency because they have high volumetric specific heat at magnetic transition temperature. Various magnetic materials such as Er_3Ni, $HoCu_2$ and $GdAlO_3$ were studied. Numazawa et al. developed ceramic gadolinium oxysulfide (Gd_2O_2S, GOS) that has an antiferromagnetic transition at 5 K in 2000's [1,2]. GOS has very high specific heat and sharp peak in comparison with Er_3Ni and $HoCu_2$ below 5 K. Ceramic GOS has high Vickers hardness. The cooling performance was much improved when GOS was used in colder side of the second stage regenerator that operated below 10 K.

Cryocoolers with magnetic regenerator materials are often used with superconducting magnet. Then, small magnetic susceptibility and specific heat insensitive to magnetic field is important in order to reduce influence of magnetic field. We measured magnetization and specific heat of ceramic GOS in magnetic field from 0 to 5 T. The magnetization of GOS represented typical temperature dependence for antiferromagnetic materials and no spin-flip transition was observed up to 5 T. As for specific heat of GOS, the peak temperature decreased from 5.5 to 5.0 K with increasing magnetic field from 0 to 5 T and the transitions remained sharp in magnetic fields. Thermal conductivity of GOS was measured in magnetic field 0 and 5 T. It was observed that the field dependence was very small. From these results, ceramic GOS was shown to be excellent magnetic regenerator material.

2. Experiments

A plate of ceramic gadolinium oxysulfide (Gd_2O_2S, GOS) was prepared and samples for various measurements are cut from this plates. Size and weights of samples are as follows: a plate of 3.89 mg for specific heat, a particle of 6.60 mg for magnetization, a rod with $5.29\times3.03\times21.8$ mm^3 for thermal conductivity, and rectangular parallelepiped of $4.81\times3.03\times21.84$ mm^3 for thermal expansion and magnetostriction. Figure 1 shows the photograph of the GOS samples used for thermal conductivity and dilation measurement.

Specific heat was measured with Quantum Design PPMS in magnetic fields of 0, 1, 3, and 5 T. Magnetization curves and temperature dependence were measured with Quantum Design MPMS. The measurements of the thermal conductivity were performed by a steady-state method with a homemade apparatus in 0 and 5 T. The temperature gradient was measured between two points on the rod sample when defined amount of heat flux was passing through the sample. The thermal conductivity was calculated with the temperature gradient, heat flux, and cross section of the sample rod in terms of Fourier's law. Thermal expansion and magnetostriction were measured using a homemade capacitive dilatometer that was installed in Quantum Design PPMS [3].

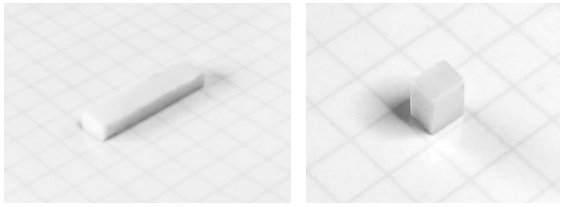

Figure 1. Photograph of GOS sample for thermal conductivity measurement (left) and magnetostriction (right).

3. Results and Discussion

3.1. Specific heat

Figure 2 shows the specific heat of ceramic GOS in 0, 3, and 5 T. Specific heat has a sharp peak at the antiferromagnetic transition temperature. The peak temperature decreased 0.2, 0.3 and 0.5 K with increasing field of 1, 3 and 5 T. This behaviour is typical for antiferromagnetic materials. The peak height was suppressed about 10% by 3 T magnetic fields but the sharpness is not varied significantly. The small transition temperature shift by magnetic field probably causes little effect on cryocooler performance, considering usual leak field of superconducting magnet. Gadolinium aluminium perovskite ($GdAlO_3$, GAP) is an antiferromagnetic material with the same rare-earth element and similar transition temperature of 3.8 K. Peak temperature of specific heat for GAP was reduced about 0.8 K by 2 T and suppression of peak height for GAP was much larger than that for GOS. In addition, peak of specific heat in GAP showed a significant broadening above 4 T. GOS has superior specific heat properties to GAP as regenerator material from the viewpoint of magnetic field effect.

The entropy of GOS was calculated from the specific heat using thermodynamic relation, $S(T) = \int_0^T \frac{C(T)}{T} dT$. Figure 3 represents the entropy of GOS in 0 T. As shown in Fig. 3, the entropy caused by magnetic spin system increases around the magnetic transition temperature. The entropy per one mole of Gd reaches about R*ln*(8), where R is gas constant. The entropy shows saturation about 15 K. This represents that almost all the spin degree of freedom for Gd (J=7/2) is released at the antiferromagnetic transition and specific heat originated from lattice is small in this temperature region.

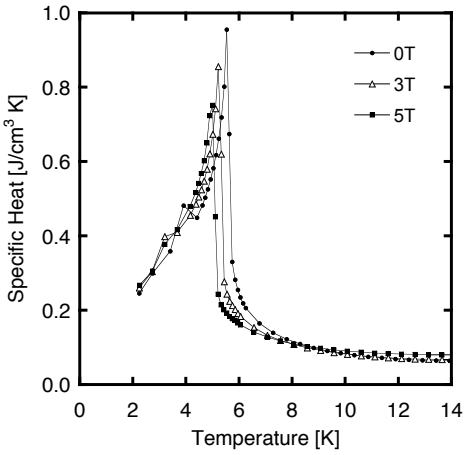

Figure 2. Specific heat of ceramic GOS in 0, 3, and 5 T.

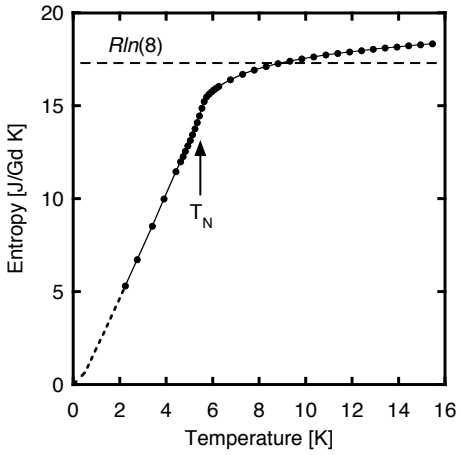

Figure 3. Entropy of ceramic GOS per one mole of Gd in 0 T.

3.2. Magnetization

Magnetization of GOS was represented as functions of temperature in 0.1, 3, and 5 T in Fig. 4. Magnetization is small and has a small peak the transition temperature as expected for an antiferromagnetic material.

Magnetization curve of ceramic GOS at 5 K was shown in Fig. 5. Those of $HoCu_2$ and ErNi at 5K [4] are plotted for comparison. Magnetization curves of GOS were measured in antiferromagnetic phase (4 K), around transition temperature (5 K), and in paramagnetic phase (6 K). There is no significant difference between them. Metamagnetic transition due to spin-flip of Gd ion wasn't observed up to 5 T in antiferromagnetic phase. Ferromagnetic ErNi has much larger magnetization than GOS. $HoCu_2$ shows spin-flip behaviour about 0.5 T. Comparing with volumetric magnetization between $HoCu_2$ and GOS, magnetization of GOS was about one third of $HoCu_2$ in 1 T.

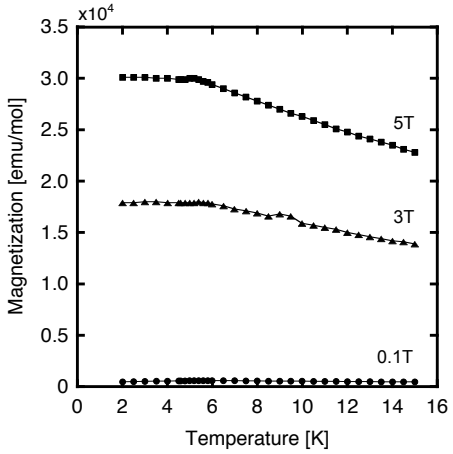

Figure 4. Magnetization of ceramic GOS as functions of temperature in 0.1, 3, and 5 T.

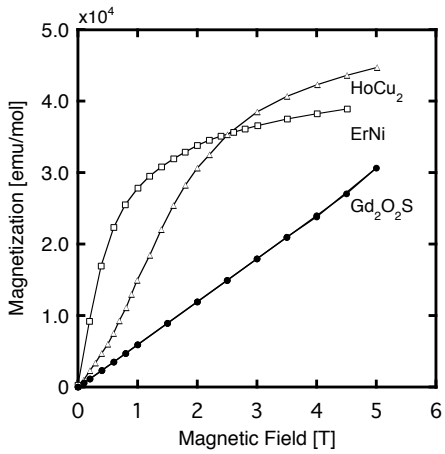

Figure 5. Magnetization curve of ceramic GOS at 5 K. Those of $HoCu_2$ and ErNi at 5K [4] are plotted for comparison.

3.3. Thermal conductivity

Figure 6 shows thermal conductivities of ceramic GOS in 0 T and some rare-earth magnetic intermetallic compounds considered as regenerator material for comparison. Thermal conductivity of GOS is comparable to those of intermetallic compounds [5, 6]. Temperature dependence of thermal conductivity of GOS was larger than those of intermetallic compounds. Thermal energy carrier difference between ceramics and intermetallic compounds may cause difference in temperature dependence.

Thermal conductivity of GOS in 0 T is close to that of dysprosium gallium garnet ($Dy_3Ga_5O_{12}$, DGG) [6]. However, DGG has large magnetic field dependence in thermal conductivity. Thermal conductivity in DGG was decreased about one order of magnitude by 5 T field. We measured thermal conductivities of GOS in 0 and 5 T and no change was observed. GOS has an advantage in thermal conductivity in magnetic field.

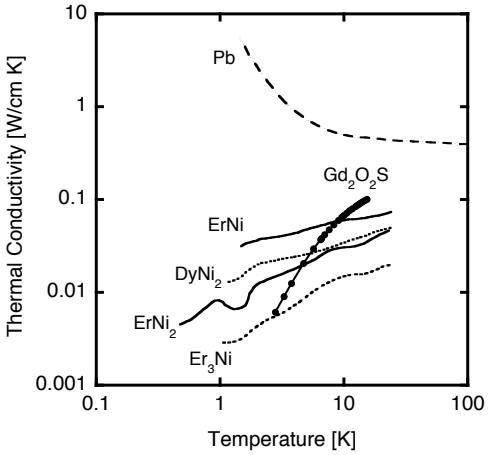

Figure 6. Thermal conductivity of ceramic GOS. Those of some rare-earth magnetic intermetallic compounds (ErNi, $DyNi_2$, $ErNi_2$, Er_3Ni) and lead [5] are plotted for comparison.

3.4. Thermal expansion and magnetostriction

Thermal contraction ($\Delta L/L$) of GOS was ~0.15% from room temperature to cryogenic temperature, that is about half of metal such as stainless steel and copper. Figure 7 shows thermal expansion of ceramic GOS below 15 K. Thermal expansion of ceramic GOS represents a slope change at the transition temperature. Additional contraction due to magnetic transition was ~10^{-4}% and much smaller than that of $ErAl_2$ that is metallic magnetocaloric material with ferromagnetic transition at 12 K [5].

Figure 8 shows magnetostriction of GOS in antiferromagnetic phase (2 and 4 K), around transition temperature (5.5 K), and in paramagnetic phase (6 K). Magnetstriction is plotted as $\frac{\Delta L}{L_{(0T)}} = \frac{L_{(B)}-L_{(0T)}}{L_{(0T)}}$. In all temperatures, GOS was expanded by magnetic field. In paramagnetic phase, magnetstriction is in proportion to squared field. In ordered phase, GOS expanded abruptly from 0 to 0.7 T. Above 0.7 T, magnetostriction showed almost same field dependence in paramagnetic phase. Magnetic domain motion is a possible reason of this large magnetostriction in low fields. $\Delta L/L_{(0T)}$ ~2×10^{-3}% by 5 T is small. We observed no damage in GOS sample after applying magnetic field several times so that magnetostriction may not cause any trouble as regenerator material.

4. Summary

We measured specific heat, thermal conductivity, thermal expansion, and magnetostriction of ceramic GOS. As for specific heat, peak temperature decreased from 5.5 to 5.0 K with increasing magnetic field from 0 to 5 T and the transitions remained sharp in magnetic fields. Thermal conductivity of GOS was enough large to be used as regenerator material and had no magnetic field dependence. Magnetostriction was shown to be small and the ceramic GOS had no damage after cyclic field application. In conclusion, ceramic GOS has excellent magnetic and thermal properties as regenerator material.

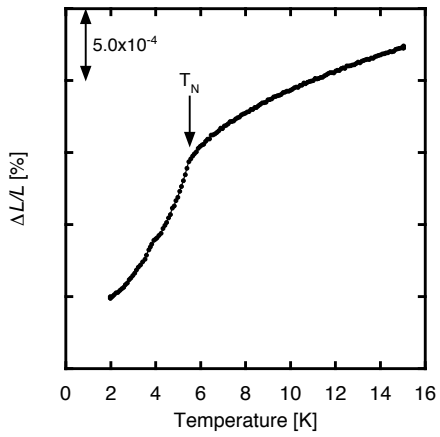

Figure 7. Thermal expansion of ceramic GOS around the transition temperature.

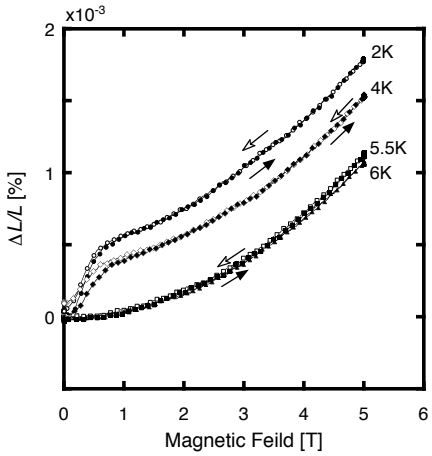

Figure 8. Magnetostriction of ceramic GOS in ordered phase (2 and 4 K), around the transition temperature (5.5 K) and para magnetic phase (6 K).

5. Acknowledgments

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