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Thermal conductivity and magnetism in $(Ca_{1-X}Sr_X)MnO_3$

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Abstract

The thermal conductivity $\kappa(T)$ and the magnetization $M(T)$ have been measured for the $(Ca_{1-X}Sr_X)MnO_3$ system ($0 \leqslant X \leqslant 0.30$). The dominant phonon scattering by magnons has been found to be essential to explain the characteristic $\kappa(T)$ enhancement below the weak-ferromagnetic (WF) transition temperature T_N. The WF behavior of $M(T)$ is weakened with increasing X and the Dzyaloshinski–Moriya interaction is indicated to be the origin of WF.

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Keywords: Thermal conductivity; $(Ca_{1-X}Sr_X)MnO_3$; Magnetization; Phonon scattering

1. Introduction

The physical properties of perovskite-type manganites $RE_{1-X}AE_XMnO_3$ (RE = trivalent rare-earth ion, AE = divalent alkaline-earth ion) have been widely investigated for the basic and applicational interests. In the electron-doped region ($X \sim 1.0$), however, the detailed reports are rather scarce. Several Ca-based $RE_{1-X}Ca_XMnO_3$ compounds have been investigated for $X \sim 1.0$, because a canted spin structure associated with pretty large negative magnetoresistance (MR) has been observed for $X \sim 0.9$ [1–3]. We have already investigated the thermal conductivity $\kappa(T)$, thermal contraction $\Delta L(T)/L$ (300 K) and magnetization $M(T)$ for the lightly electron-doped $La_{1-X}Ca_XMnO_3$ ($0.98 \leqslant X \leqslant 1.0$) system [4]. $\kappa(T)$ of $CaMnO_3$ showed a peculiar enhancement below the weak-ferromagnetic transition temperature T_N (= 130 K). The $\kappa(T)$ enhancement was rapidly suppressed by introduction of Mn^{3+} spins due to the La^{3+} doping and/or the introduction of oxygen deficiency. The reduction of the $\kappa(T)$ enhancement could not be explained by the difference in the lattice states as monitored by $\Delta L(T)/L$ and we examined the possibility of the magnon heat conduction below T_N. In order to perform detailed analyses of the origin of the $\kappa(T)$ enhancement, we must collect more detailed information about the related compounds. In this paper, we investigate $\kappa(T)$ and the magnetization $M(T)$ for the $(Ca_{1-X}Sr_X)MnO_3$ system ($0.0 \leqslant X \leqslant 0.30$). The substitution of the Ca^{2+}-site by the larger Sr^{2+} ions is expected not to change the spin state of Mn^{4+} ions but to reduce the overall structure deviation from cubic and introduce lattice randomness.

2. Results and discussion

$(Ca_{1-X}Sr_X)MnO_3$ samples were prepared from stoichiometric mixtures of $CaCO_3$, $SrCO_3$, La_2O_3 and Mn_3O_4 raw powders. The mixtures were calcined twice at 1000°C for 24 h in air, pressed into pellets and then sintered at 1450°C for 8 h in air. The samples were heat-treated at 1100°C for 24 h in flowing oxygen to improve the oxygen stoichiometry. All the samples were confirmed to be in a single orthorhombic phase at room temperature by means of X-ray diffraction. The density of each sample was about 85% of the ideal one. The thermal conductivity $\kappa(T)$ was automatically measured in a Gifford–McMahon cycle helium refrigerator as described elsewhere [5]. The magnetization $M(T)$ was measured by a SQUID magnetometer under a magnetic field of 0.5 T after zero field cooling (ZFC).

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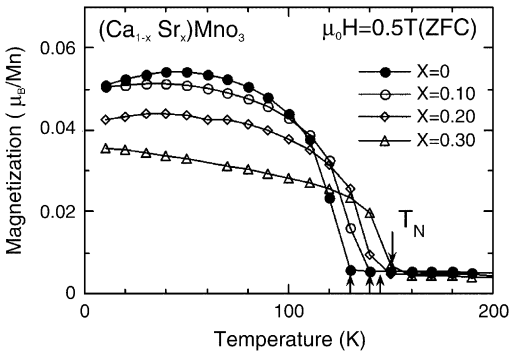

Fig. 1. Temperature dependence of the magnetization $M(T)$ for the $(Ca_{1-X}Sr_X)MnO_3$ system.

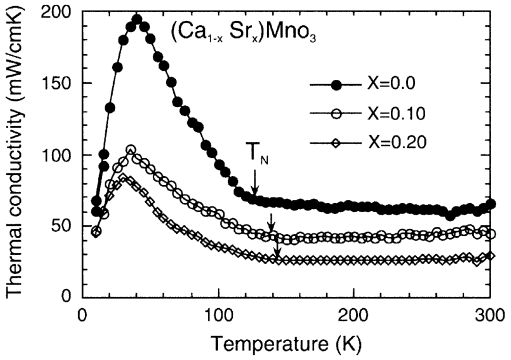

Fig. 2. Temperature dependence of the thermal conductivity $\kappa(T)$ for the $(Ca_{1-X}Sr_X)MnO_3$ system.

Fig. 1 shows the magnetization $M(T)$ for the samples. The $M(T)$ curve of the $X = 0.0$ sample shows a sharp increase at $T_N = 130$ K, which suggests the onset of the weak ferromagnetism (WF) [6]. The magnitude of the WF moment is about 1/80 of the Mn^{4+} moment ($\sim 3\ \mu_B$). T_N gradually increases with increasing X; e.g., $T_N = 140$ K for $X = 0.10$ and $T_N = 150$ K for $X = 0.30$, respectively. In contrast, the WF moment decreases with increasing X.

$(Ca_{1-X}Sr_X)MnO_3$ with orthorhombic structure has no inversion symmetry at the midpoint of the nearest Mn^{4+} spins. In this lattice, Dzyaloshinski–Moriya (DM) antisymmetric exchange interaction is possible, which results in WF with a canted spin configuration in an antiferromagnet [7]. The substitution of Ca^{2+} sites by the larger Sr^{2+} ions should bring about the decrease of tilting of the MnO_6 octahedra and the local symmetry between nearest Mn^{4+} spins approaches cubic. This effect weakens DM interaction and may enhance the antiferromagnetic superexchange interaction, which results in the decrease of the WF saturation value of $M(T)$ and increase of T_N.

Fig. 2 shows $\kappa(T)$ vs. T. With decreasing temperature, $\kappa(T)$ of all the samples remains almost constant down to T_N, where $\kappa(T)$ abruptly begins to increase. The $\kappa(T)$ enhancement below T_N is far drastic for the $X = 0.0$ and is weakened with increasing X. With further decrease of T, $\kappa(T)$ takes a sharp maximum at T_{max} (~ 40 K for $X = 0.0$). T_{max} slightly decreases with increasing X, i.e., with decreasing $\kappa(T)$ of each specimen.

Now let us briefly discuss the origin of the $\kappa(T)$ enhancement. Since the semiconductive electrical resistivity $\rho(T)$ of the present sample is very large ($\rho > 1\ \Omega$ cm), the electron component κ_e can be entirely neglected. As inferred from $M(T)$ in Fig. 1, 10% Ca^{2+}-site substitution by Sr^{2+} hardly affects the magnetic order below T_N, while $\kappa(T)$ enhancement is drastically depressed in the $X = 0.10$ sample. This result suggests that the enhancement is unlikely to be related with the magnon heat transfer. Then the phonon component κ_{ph} should be dominant over the entire temperature range.

In insulators, the phonon–phonon scattering is well-known to result in the κ_{ph} peak at a low temperature and $\kappa_{ph} \propto 1/T$ dependence at higher temperatures [8]. The $1/T$ dependence, however, does not explain our observation, because $d\kappa(T)/dT$ discontinuously changes around T_N. The temperature dependence of $\kappa(T)$ of $(Ca_{1-X}Sr_X)MnO_3$ is consistent with the κ_{ph} model with dominant phonon scattering by magnons below T_N. The overall reduction of $\kappa(T)$ and the slight decrease of T_{max} with increasing X can be understood as to come from enhanced phonon scattering of point defect-type caused by the Ca^{2+}-site substitution [9], while the strength of the magnon scattering preserving nearly constant (detailed numerical analyses are to be presented elsewhere).

In summary, we have analyzed the effect of Ca^{2+}-site substitution by Sr^{2+} on the behavior of $M(T)$ and $\kappa_{ph}(T)$ in $(Ca_{1-X}Sr_X)MnO_3$. The weak ferromagnetism was weakened with increasing X as a result of the reduction in the orthorhombic lattice distortion from cubic. The origin of the apparent $\kappa(T)$ enhancement below T_N can be attributed to the phonon scattering by magnons, which rapidly decreases with decreasing temperature.

References

[1] W. Bao, et al., Phys. Rev. Lett. 78 (1997) 543.
[2] C. Martin, et al., J. Solid State Chem. 134 (1997) 198.
[3] H. Chiba, et al., Solid State Commun. 99 (1996) 499.
[4] H. Fujishiro, et al., J. Phys. Soc. Jpn. 69 (2000) 2082.
[5] M. Ikebe, et al., J. Phys. Soc. Jpn. 63 (1994) 3107.
[6] J.B. MacCesney, et al., Phys. Rev. 164 (1967) 779.
[7] E.A. Turov, Physical Properties of Magnetically Ordered Crystals, Academic Press, New York and London, 1965.
[8] G.A. Slack, Solid State Phys. 34 (1978) 1.
[9] P.G. Klemens, Solid State Phys. 7 (1958) 1.