Anomalous Transport Properties of n-$CdCr_2Se_4$ Single Crystals Near the Curie Temperature

By

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Abstract

Anomalous increases of the thermoelectric power (the Seebeck coefficient α) and the thermal conductivity κ in n- type $CdCr_2Se_4$ single crystals are found near the Curie temperature T_c. The temperature dependences of the magnetic moment μ_B^* and the dipolar spin-spin relaxation time τ_s near T_c suggest that these effects can be attributed to a magnon drag.

1. Introduction

Several studies on the chalcogenide spinel $CdCr_2Se_4$, showing a large variety of magnetic and electrical properties, have been worked out by various authors.[1)~3)] It was reported, for example, that the magnetoresistance indicated pronounced negative maxima at the Curie temperature $T_c=130$ K.[4)] In addition, the Seebeck coefficient in n-type hot-pressed samples has been investigated in detail under the application of a magnetic field H; and the behavior was explained by a multi impurity band model.[5),6)] However, since the Seebeck coefficient of $CdCr_2Se_4$ has been investigated so far only in polycrystalline forms, an accurate mechanism in respect of thermoelectric transport properties, especially near T_c, is not known yet. In order to know the dynamic transport properties at the Curie temperature, polycrystals are less available than single crystals. The reason is that collisions of charge carriers, caused by many grain boundaries or crystal disorders[7)] in the polycrystal lattice, are probably responsible for an interruption of their transport in this transition temperature region.

To prevent this problem, more refined investigations were made in the case of

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good quality single crystals of n-type $CdCr_2Se_4$. This paper summarizes some of the experimental results on the Seebeck coefficient α, the magnetoresistance $(\Delta\rho/\rho_0)$, and the thermal conductitiy κ. Further, the experimental results on the magnetic moment μ_B^* vs T and the spin relaxization time τ_s, which were measured in order to account for their transport properties, are summarized.

2. Experimental results and discussions

Used n-type samples were prepared by annealing high-quality p-type single crystals, which were grown by the known flux method, in a closed vapor of indium at 500°C with varying times. Fig. 1 shows the dependence of the Seebeck

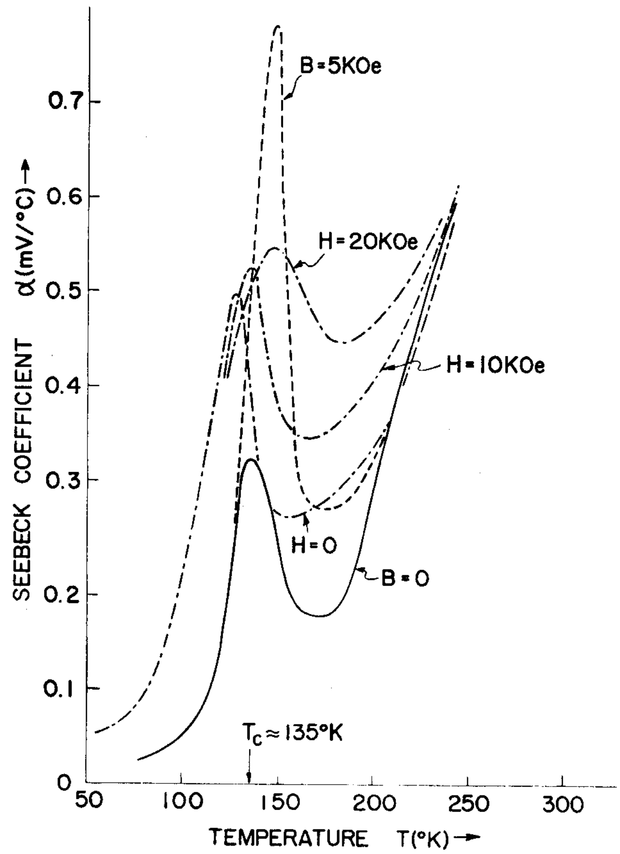

Fig. 1. The Seebeck ccefficient α as functions of temperature T and external magnetic field H for a high-quality single crystal of n-type $CdCr_2Se_4$. The heavy solided and dashed curves correspond to the single crystal, and the result for a hot-pressed polycrystalline sample[5] is indicated by the light dot-dashed curves.

coefficient α on T and H measured on a typical sample, whose annealing time was 39 minutes at 500°C. Its electron concentration was approximately $6\times10^{12}cm^{-3}$. In this figure, Smith's data for the case of a hot-pressed sample ($n\approx3\times10^{17}m^{-3}$) is compared with the present data.

From such data, it is clearly found that the properties of the single crystal differ from the results of the hot-pressed polycrystal in several important respects. For example, (1) the absolute value of α in the polycrystal is approximately twice that of the single crystal. Neverthless, the electron concentration of the polycrystal exceeds that of the single crystal by a factor of 10^4. The result is the opposite effect of that where a lower value of α would be expected from the normal diffusion theory.[8] (2) Under the application of a magnetic field $H=5$ KOe, a sharp rise of α_H occurs near the Curie temperature T_c only in the case of the single crystal. On the other hand, in the polycrystal, an increase of α_H is found at 150 K, where the resistivity shows a maximum. For example, the peak value of α_H in the single crystal at $H=5$ KOe is 2.4 times as great as that of α_0 at $H=0$, and that of the polycrystal is barely 0.1 times even in the case of $H=20$ KOe. The contrast can be mostly attributed to a difference of grain boundaries and imperfections contained in each crystal.

It is noted, however, that the maxima of α_0 of these samples were observed in the vicinity of T_c. Regarding this peak of α_0, it has been previously pointed out by A. Amith and G. L. Gunsalus that there was no simple relation among the dependence of α, the resistivity ρ and the normal Hall coefficient R_H on T and H. In order to explain the result, two impurity bands showing a different contribution of conduction electrons and holes with varying temperatures have been considered.[5),6)] However, as to whether the anomalous peak of α_0 is to be ascribed only to the presence of these two impurity bands, it is difficult to say. Our result on α_H as well as on α_0, which peaked sharply in the vicinity of T_c, probably accounts for the difficulty of this two band model. It was also confirmed in the single crystals that the carrier transport of the thermoelectric power differed from those of ρ and R_H. As a result the anomalous peaks of α_0 and α_H can be probably attributed to a characteristic phenomenon arising from a very great interaction between charge carriers and magnetic spins at the Curie temperature.

To check this possibility, measurements on the magnetoresistance ($\Delta\rho/\rho_0$), which was even after the effects of spin disorder scattering[9] and the spin splitting of the conduction band,[10] were first made on the same sample. Then, a measurement on the thermal conductivity κ was also made in order to reveal what was responsible for the anomalous diffusion of the charge carriers at T_c. In Fig. 2, the result of ($\Delta\rho/\rho_0$) at $H=5KOe$, and those of the resistivity factors ρ and ρ_0 (at H

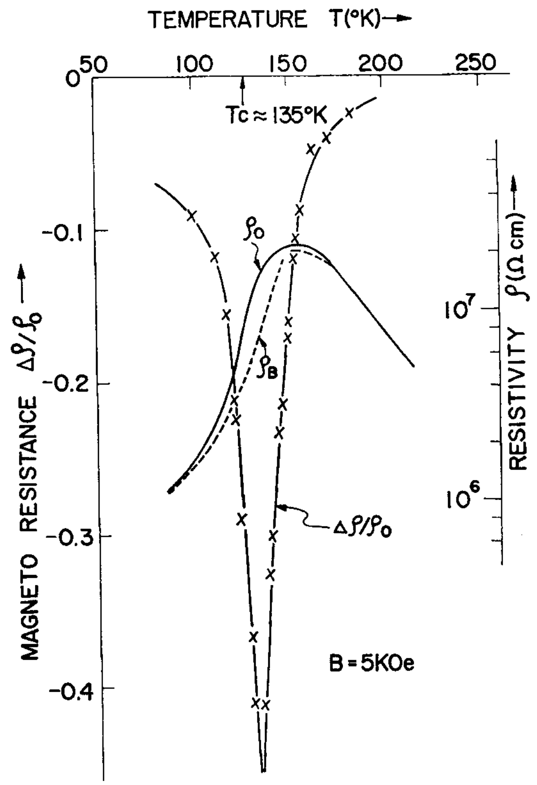

Fig. 2. Temperature dependences of magnetoresistance $\Delta\rho/\rho_0$ and resistivities ρ_0, ρ_H corresponding to the absent and the presence of H for n-type $CdCr_2Se_4$ single crystal.

$=0$) are shown, respectively. Also, the result of κ vs T is shown in Fig. 3, where it was mainly measured on a limited case of $H=0$ because of the difficulty of the experiment by using a static differential method.

These results suggest that there may be some close correlation among the three peaks of α, $(\Delta\rho/\rho_0)$ and κ, occurring near T_c. The large negative resistance is caused by the interaction of charge carriers with magnetic spins, and therefore, the interaction is likewise responsible for the anomalous diffusion of the conduction carriers on α and κ. Unless one considers a contribution of the momentum from the spin system to the thermally excited carriers (electrons) through the diffusion process, it is difficult to explain their anomalous rises.

Similar behaviors have been observed in non-magnetic semiconductors, e. g. *Ge*, and those have been known as the phonon drag.[11] Furthermore, the anomalous rise of α near T_c has been also observed in $MnTe$[12] and $FeCr_2S_4$[13]; and the effect was qualitatively explained in terms of a magnon drag. This later effect arises from

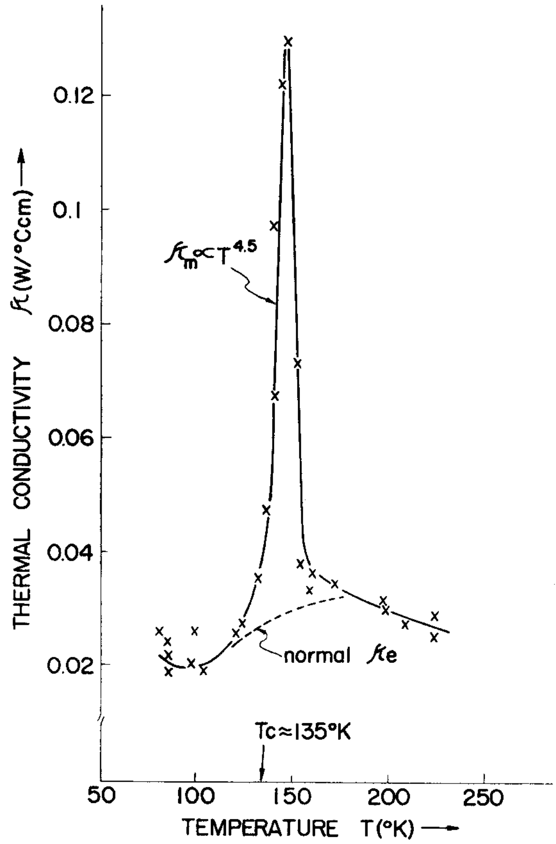

Fig. 3. The thermal conductivity κ vs T for n-type $CdCr_2Se_4$ single crystal. The dashed curve presents the normal κ_e acquired by electrons, which follows generally from $\kappa_e=2(k_B/e)T\ \sigma_0$ (where σ_0 is the conductivity at $H=0$).

the strong coupling between the charge carriers and the spin waves (magnon), through which the carriers are dragged along a temperature gradient. Consequently, this magnon model satisfactorily accounts for the contradictory data where the value of α_H exceeded that of α_0, though the density of the conducting electrons increased greatly near T_c by an applied H.

It is important to decide whether or not the magnon drag is actually occurring in the vicinity of T_c of the n-type $CdCr_2Se_4$ single crystal. In order to check the occurrence closely, measurements on the non-elastic scattering of neutrons,[14] or a spin resonance of its thin film, have to be taken. However, it is quite possible to expect the magnon drag from the fact that the magnetic shortrange ordering of this material occurred up to 150 K.[15] Also, a thermal spin fluctuation of a long wavelegnth was observed near T_c for normal ferromagnetic materials.[16] Therefore, in the following arguments, we assume a long wavelength magnon ascribing to such the spin fluctuation as a preliminary step. Then, we check whether or not that is consistent with the present data.

The Hamiltonian denoting the exchange interaction between the spins s of a charge carrier (conduction electron) and the localized magnetic spin S_n of a C_r^{3+} ion of this material is written as

$$\mathscr{H}'_{int} = -\sum_n J(r-R_n)s\cdot S, \tag{1}$$

where $J(r-R_n)$ gives the interaction as a function of the distance $(r-R_n)$ between them, J is an exchange integral, n is the position index of each magnetic ion and $\sum_n$ denotes the sum of the total magnetic spins. The known spin-splitting of the conduction band and the spin-disorder scattering in a magnetic semiconductor are a consequence of this interaction, as pointed out by several authors.[17),18)]

On the other hand, the energy interval $\mathscr{E}_c^{\pm}$ due to the interaction $\mathscr{H}'_{int}$ is given by

$$\mathscr{E}_c^{\pm} = -\frac{J_k}{N}\sum_{n,\gamma} W_\gamma \langle \Psi_k \pm \gamma \,|\, \mathscr{H}'_{int} \,|\, \Psi_k \pm \gamma \rangle = \mp \frac{J_k}{2} S\left(\frac{M}{M_s}\right), \tag{2}$$

where $J_k = N\int d^3r\,|u_k(r)|^2 J(r-R_n)$ is an exchange integral to electrons having a wave vector k, $u_k(r)$ is the periodic function part in Bloch's function $\Psi_k(r) = u_k(r)\exp(ik\cdot r)$, and r represents eigen-vectors of the Hamiltonian corresponding to the localized magnetic spins. Then, W_γ is their occupation probability, N is their number per unit cell and M is the total magnetization, depending on T and H. Further, M_s is the suturation magnetization given as $Ng\mu_B S$ (g is the Lande constant) and μ_B is the Bohr magneton, respectively.

This band-splitting accompanied by the spin-splitting will serve to elucidate the magnon drag model. Namely, a situation of the thermally excited magnon is generally proved from a direct measurement of $\mathscr{E}_c^{\pm}$ by means of an electron spin resonance or from a change of M vs T at the transition temperature where the spin-flipping and the spin-disorder scattering are possible. The latter case is based on the fact that a decrease of M (i. e., a value of ΔM) practically amounts to a presence of magnons by $g\mu_B\sum_q b_q^+ b_q$ per unit cell (where b_q^+, b_q are a creation operator and an annihilation operator having a wave vector q for each magnon). In addition, an average density of the magnon (i. e., $\langle n_q\rangle = \langle\sum_q b_q^+ b_q\rangle$), in general, changes according to the Bose distribution function, $\langle n_q\rangle = \{\exp(\beta\hbar\omega_q)-1\}^{-1}$, where $\beta = 1/k_B T$, k_B is the Boltzmann's constant, and $\hbar\omega_q$ is the energy of one of the magnons having an angular frequency ω_q. In the case of a single magnon process, the dependence of

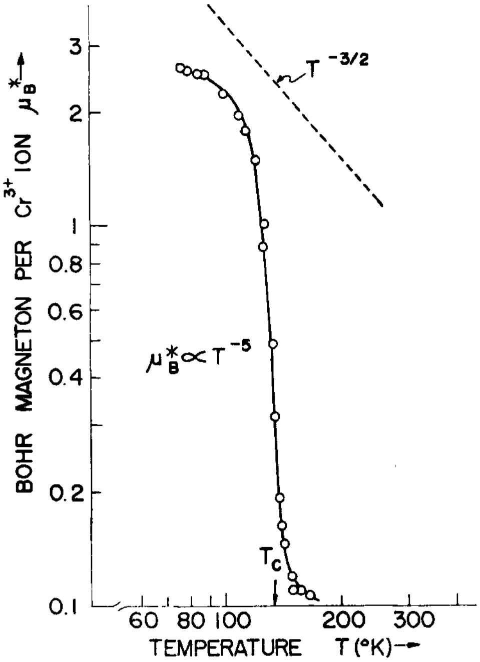

Fig. 4. The temperature dependence of the magnetic moments μ_B^* on a log scale of n-type single crystal for an applied magnetic field of 0.5 KOe. The dashed line represents the variation of μ_B^* corresponding the single magnon process.

ΔM on T should follow the known Bloch's rule, i. e., $\Delta M \propto T^{3/2}$, if the condition $\hbar\omega_q \gg k_B T$ is satisfied.

For the sake of a comparison with this dependence, measurements on n-type single crystals were performed near T_c by means of a magnetic balance. The result is shown in Fig. 4, where, for convenience, the values of M are given by a form of the Bohr magneton per Cr^{3+} ion as compared with other data.[19),20)] From a slope of the curve, it was revealed that the magnetic moment follows $T^{4.5}$ near T_c, and that this value is far greater than $T^{3/2}$ for the single magnon process. Consequently, it would be expected that the thermal excitation of the magnon near T_c was ascribed to at least a double-magnon process due to a magnon-magnon interaction. The reason for this is that the result of $\Delta M \propto T^4$ was found in a calculation taking account of the interaction between magnons,[21)] and that our result is in reasonable agreement with the result calculated by using an averaeg value due to a reflection toward the adjacent spin $S_{j+\delta}$ of the magnetic spin S, i. e., $\bar{S} = \langle S_j \cdot S_{j+\delta} \rangle / S$.[22)] The latter is particularly important near T_c, because every spin leads to the strong thermal fluctuation in this temperature range as mentioned above.

In such a spin system where there occurs a magnon-electron interaction through the $s \cdot S$ spin vector dot product in Eq. (1) have to be taken into account. Namely, by using exchange terms in the perturbation of the Coulomb and Hartree-Fock equation, the Hamiltonian $\mathscr{H}'_{int}$ in Eq. (1) needs to be written as[23)]

$$\mathscr{H}'_{int} \rightarrow \sum_{ss'kk'q} C_{ks}C_{k's'} \left[b_q J_{kk',q} SS' + b_q^+ J_{kk',q} SS' \right]$$
$$+ \sum_{kk',q} J_{kk',qq'} b_q b_{q'}^+ \left[C_{k+} C_{k'-}^+ - C_{k-} C_{k'-}^+ \right], \quad (3)$$

where the C_{ks}^+'s are the creation operators for the electrons of the wave vector k, and the b_q^+'s are the operators for the magnons of the wave vector q. The first part indicates the single magnon process, and the second part indicates the double magnon process, respectively. To search for a close solution, therefore, an analysis inclusive of the second term is required. However, translating this calculation into practice is very difficult.

On the other hand, from a slope of the thermal conductivity, we can also expect the κ vs T curve, as shown in Fig. 3. In non-magnetic materials, a specific heat C_v in a fixed area follows $C_v \propto T^3$ at a lower temperature than the Debye temperature.[24)] Although it is undesirable to accept the phonon-electron process without reserve into the magnon-electron process, the magnon drag model is analogous to the phonon drag model as far as $T < T_c$ is satisfied.[25)] Provided that there is the drag of electron from a high temperature edge to a low temperature edge through the single magnon process, the thermal conductivity κ should follow the known T^3 low below T_c. Actually, it was revealed that κ as well as ΔM also approximately followed $\kappa \propto T^{4.5}$. Therefore, this result is accounted for by the double magnon process.

The possibility of the double magnon model arises from the following reasons. when a thermal current flow U, corresponding to an excitation of traveling spins: is given for each magnetic ion as

$$U = \sum_q \hbar\omega_q (\nabla_q \omega_q), \quad (4)$$

the group velocity $\nabla_q \omega_q$ of the magnon is able to be approximated as $(\Lambda/L)\bar{v}_m$ signifying its mean velocity $\bar{v}_m$, its mean free path Λ and a sample length L. Hence, Eq. (4) is rewritten as

$$U \simeq [\hbar\omega_q(T_h) - \hbar\omega_q(T_c)] \bar{v}_m \Lambda / L. \quad (5)$$

In addition, taking notice that the bracketed energy difference in Eq. (5) equals $C_v(T_h - T_c)$, Eq. (5) is simplified to $U = C_v \Lambda \bar{v}_m \Delta T / L$ (where $\Delta T = T_h - T_c$). On the other hand, there is a relation of $U = \kappa \Delta T / L$ between κ and the thrmal capacity U flowing through a unit area per unit time, and so the thermal conductivity κ is given by

$$\kappa = C_v \Lambda \bar{v}_m. \qquad (6)$$

In Eq. (6), it is clearly indicated that, if $T < T_c$, the temperature dependence of κ mostly follows that of C_v, because $\bar{v}_m$ is considered as a constant value. Λ is quite long for reason that the collisions of magnons due to imperfections of the crystal lattice are independent of T. Further, the sharp drop of κ occurring at the temperature range $T > T_c$ comes mainly from a decrease of Λ through the *Umklapp* process[26] and the collisions between the magnons.

To better clarify the situation of the magnons, measurements of the relaxation time τ_s relating to the $s \cdot S$ interaction were performed by means of an X-band ESR spectrometer. Fig. 5 shows the peak to peak line-width $\Delta H_{1/2}$ and τ_s vs T measured on about 0.8 mm highly polished spheres. The curve of τ_s is calculated from $\tau_s = g\mu_B\pi\Delta H_{1/2}/\hbar$ by using g-values and $\Delta H_{1/2}$ corresponding to respective temperatures. Further, it should be added that the result for $\Delta H_{1/2}$ was in fairly good agreement with that of LeGraw, Philipsborn and Sturge.[19]

From the curve of τ_s, it is found that the spin relaxation time decreases sharply

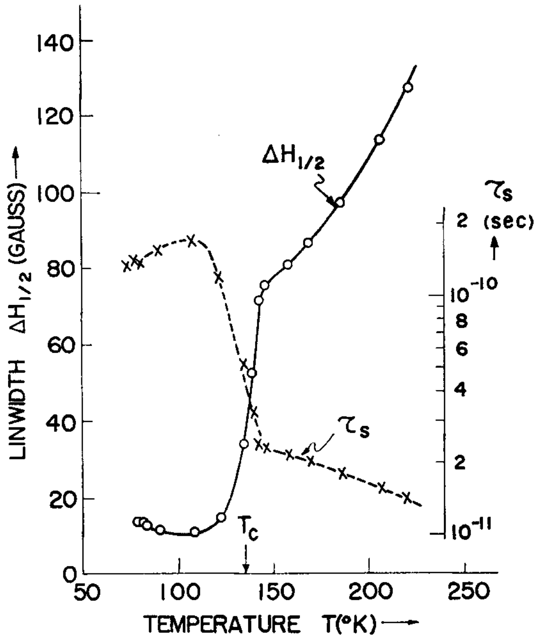

Fig. 5. Temperature dependences of the peak to peak linewidth $\Delta H_{1/2}$ obtained from the ESR spectra and the spin relaxation time τ_s vs T for about 0.8mm spheres of the n-type $CdCr_2Se_4$ stngle crystal.

in the narrow temperature range from 100K to 150K. This property offers two important sources of information for the explanation of the magnon-electron coupling.

First, it is possible to estimate at situation of the exchange interaction between localized Cr^{3+} ions. Namely, by using an approximate equation in the molecular field theory, i. e. $\Delta H_{1/2} \simeq \mu_B^{*}/r_{12}^3$ (where r_{12} is the distance between the nearest adjacent $Cr^{3+}-Cr^{2+}$ ions, μ_B^* is a magnetic moment at a given temperature), an extension of $\Delta H_{1/2}$ is easily identified. For example, taking a view of a super exchange path in a $Cr^{3+}-Se^{2-}-Se^{2-}-Cr^{2+}$ cohesion through In^{3+} ion, we get the result $\Delta H_{1/2} \simeq 27$ Gauss at T_c by using $r_{12} = (\sqrt{8}/4) \cdot a$ (where a is the lattice constant and 10.72Å) and $\mu_B^* = 1.25\mu_B$, which is given in Fig. 4. This value is very close to that of $\Delta H_{1/2} \simeq$ 30 Gauss, measured directly at T_c on the line width (see Fig. 5). In attempting to calculate $\Delta H_{1/2}$ for the case of the 90°-path relating a $Cr^{3+}-Cr^{2+}$ cohesion, its solution results in $\Delta H_{1/2} \simeq 220$ Gauss, so that this direct coupling evidently does not come into existence.

Next, it is possible to know a degree of the electron-magnon interaction from a change in the relaxation time τ_s. As shown in Fig. 5, τ_s decreases rapidly with an increase of temperatures ranging from 100 K to 150 K. This is because the localized magnetic fields of adjacent unpaired electrons have a perturbation through the thermal fluctuation of magnetic spins, i. e., long-wavelength magnons, occurring near T_c. The change of τ_s in the temperature range is clearly distinguishable from that at 150 K, in which their localized fields are perfectly at random.

On the basis of these experimental facts, it is concluded that the marked increase of the Seebeck coefficient arises from the anomalous diffusion of thermally excited electrons due to the magnon rather than the contribution of two impurity bands. From the measurements of the thermal conductivity and the magnetization as a function of temperatures, the electron-drag owing to the coupling with double magnons can be expected as a reasonable possibility. The electron transport in the transition temperature region is subject to the influence of grain boundaries or imperfections of the crystal lattice. Hence, it seems inevitable that single crystals of as good a quality as possible should be used. To better clarify the feasibility of the magnon drag model, measurements on the frequency ω_q of the thermal excited magnons and on the thermal conductivity κ at the applied magnetic field may need to be performed. A theoretical analysis taking into account the double magnon process is now in progress.

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