On the Behavior of Thermal Conductivity near the Magnetic Transition Point

Kyozi KAWASAKI

Department of Applied Physics, Faculty of Engineering
Nagoya University, Nagoya

The anomaly of thermal conductivity at the magnetic transition point observed in certain magnetic crystals has been treated theoretically using the correlation function expression for the thermal conductivity. The heat conduction by the spin system is shown to be negligible in the vicinity of the transition point. The phonon thermal conductivity was studied when the transition temperature is much smaller than the Debye temperature adopting a simple spin-phonon coupling derived by a consideration of the change of energy of the spin system caused by the strain due to a phonon. Processes involving creation and annihilation of a phonon as well as scattering have been considered, and the anomalous temperature dependence of thermal conductivity at the transition point was understood in terms of the critical scattering of phonons by critical fluctuations of the energy density of the spin system which is revealed in the specific heat of the spins. Cases with more general types of the spin-phonon interaction are briefly discussed.

§ 1. Introduction

In recent years, anomalies in the thermal conductivity at the magnetic transition point have been observed in some magnetic crystals such as MnO, CoO,[1] CoF_2, MnF_2,[2] Fe_3O_4,[3] UO_2,[4] $CuCl_2 \cdot 2H_2O$, and $CoCl_2 \cdot 6H_2O$.[5] Although such anomalies are generally attributed to the effect of spin ordering reflected through the spin-phonon coupling, no theoretical treatments have been given so far. A primary purpose of the present paper is a theoretical understanding of these phenomena. The problem can conveniently be divided into two aspects: (1) the precise determination of the spin-phonon coupling in each of these crystals, and (2) understanding of the anomalies with this spin-phonon coupling. Here we shall be mainly concerned with this second aspect. Because of the lack of the precise knowledge about the spin-phonon coupling and in order to avoid too much complications which make the problem untractable, we shall assume a simple spin-phonon coupling and furthermore restrict ourselves to the case where the magnetic transition temperature is much smaller than the Debye temperature, and we analyze it in detail. In this simple case the anomaly is understood as a critical scattering of phonons by critical fluctuations in the energy density of spins. As a numerical example, the case of CoF_2 was studied and a qualitative agreement with the experiment was obtained. More general

cases present considerable difficulties, and are discussed only briefly.

In this study, we start from the correlation function expression for thermal conductivity due to Kubo, Mori and others,[6] which is expressed as

$$\kappa = \frac{1}{2k_B T^2 V} \int_{-\infty}^{\infty} \langle \{Q(t), Q\} \rangle dt, \qquad (1\cdot1)$$

where Q denotes the total heat flux operator, $\{\cdots\}$ the symmetrized product, $\langle\cdots\rangle$ the ensemble average, and V the volume occupied by the system.

§ 2. Thermal conductivity due to the spin system

It has been pointed out and has actually been observed that in some ferromagnetic crystals, there is an appreciable contribution from the spin system to the thermal conductivity at low temperatures,[7],[8] where the mean free paths of magnons and phonons become comparable. As the temperature rises, the interaction between magnons reduces the magnon mean free path rapidly, and in the vicinity and above the transition point, the concept of magnons completely loses its meaning. Thus the previous treatments of the thermal conductivity due to the spin system,[7] where the heat is supposed to be carried by magnons which are scattered occasionally, should be modified completely at the temperatures of our interest.

This is a typical example of a non-Boltzmann type transport phenomena,[9] and it is most convenient for this treatment to use the correlation function expression (1·1) for the thermal conductivity, where we substitute for Q a heat flux operator due to the spin system Q^s.

In order to find an explicit form of Q^s, we shall make use of the energy conservation law ignoring the interaction of the spin system with other systems such as the lattice, which is permissible except for very low temperature. The law of energy conservation is written in terms of the Fourier components as follows:

$$i\mathbf{k} \cdot Q_k^s = \dot{H}_k^s, \qquad (2\cdot1)^*$$

where H_k^s and Q_k^s are the Fourier components of the Hamiltonian density and the heat flux density operators of the spin system, respectively, and for the Heisenberg spin system we have

$$H_k^s = -\frac{1}{N} \sum_q J(q)\, \mathbf{S}_{q+k/2} \cdot \mathbf{S}_{-q+k/2}, \qquad (2\cdot2)$$

where $J(q)$ and $\mathbf{S}_q$ are the Fourier components of the exchange interaction and the spin density operator respectively, N being the total number of the lattice points. The heat flux operator Q^s is the limit $k \to 0$ of Q_k^s obtained from $(2\cdot1)$.

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*) The dot means the differentiation with respect to time.

The result is

$$Q^s = \frac{1}{N^2} \sum_q \sum_p \{ \nabla J(p) J(q, p-q) + \nabla J(q) J(p, q-p)$$
$$- \nabla J(q-p) J(q, p) \} S^+_{q-p} S^0_{p} S^-_{-q}, \qquad (2\cdot3)$$

where we used the following notations:

$$\nabla J(q) = \partial J(q)/\partial q, \quad J(q, p) = J(q) - J(p), \quad \tilde{A} = A - \langle A \rangle.$$

In the spin wave region, it is easy to verify that (2·3) reduces to the correct heat flux operator of magnons,

$$\sum_q \frac{\partial \epsilon_q}{\partial q} \epsilon_q b^*_q b_q$$

with the magnon spectrum $\epsilon_q = 2SJ(0, q)$ and the magnon operators b_q and b^*_q.

In view of the difficulty of calculating the time-displaced correlation function of the heat flux operator, it is most convenient to regard the heat conduction as a diffusion of heat, where the diffusion constant is given by $D^s = \kappa^s/C^s$ with the heat capacity per unit volume C^s. Use of the fluctuation-dissipation theorem and (2·1) yields the following expression for D^s:

$$D^s = \lim_{k \to 0} \int_{-\infty}^{\infty} dt (\dot{H}_k(t), \dot{H}^*_k)/2k^2 (H_k, H^*_k), \qquad (2\cdot4)$$

where

$$(A, B) = \int_0^\beta \langle e^{\lambda H} A e^{-\lambda H} B \rangle d\lambda.$$

This is the same with the expression for the spin diffusion constant except for S_k replaced by H_k.[9] The same discussion as in references 9) and 10)[*] shows that the critical fluctuation at the transition point appears only in the denominator of (2·4), which is for $k=0$ proportional to the specific heat C^s. The numerator of (2·4), and hence κ^s involves only the short range correlations and thus is expected to show a mild temperature dependence coming from the temperature dependence of the short range order, which we shall consistently neglect in this paper. Thus we have estimated $T^2\kappa^s$ in the high temperature limit, and obtained

$$\kappa^s = \frac{\tau}{3k_B T^2 V} \langle Q^s \cdot Q^s \rangle_\infty, \qquad (2\cdot5)$$

where τ is the microscopic relaxation time associated with the heat flux operator Q^s, $\langle \cdots \rangle_\infty$ the ensemble average taken in the high temperature limit.

When we assume the single exchange interaction J between the nearest neighbor spins, we have

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[*] See in particular the discussion on the page 981 of reference 10).

$$\langle \boldsymbol{Q}^s \cdot \boldsymbol{Q}^s \rangle_\infty = \frac{8}{9} b^2 N S^3 (S+1)^3 (zJ^2)^2, \tag{2.6}$$

where z is the number of the nearest neighbors and b the distance between the nearest neighbors. τ could be obtained in the same way as in reference 9) assuming a Gaussian decay for $\langle \boldsymbol{Q}^s(t) \cdot \boldsymbol{Q}^s \rangle$ and calculating $\langle \dot{\boldsymbol{Q}}^s \cdot \dot{\boldsymbol{Q}}^s \rangle$. However, for a rough estimation of κ^s, it is sufficient to substitute for τ that obtained for the spin diffusion constant,[9] namely,

$$\tau^{-2} = \frac{8}{3} \xi S (S+1) z J^2, \quad \xi = 1 - \frac{39}{5z^2} \left\{ 1 + \frac{3}{26 S(S+1)} \right\}. \tag{2.7}$$

Thus the expression for κ^s becomes

$$\kappa^s = 8 N \tau b^2 S^3 (S+1)^3 (zJ^2)^2 / 27 k_B T^2 V. \tag{2.8}$$

If we assume the molecular field theory to relate J to the magnetic transition temperature T_0,

$$T_0 = 2z |J| S(S+1) / 3k_B. \tag{2.9}$$

we obtain at the transition point and for the b.c.c. lattice

$$\kappa^s = 9 \tau k_B^3 T_0^2 / 4 a h^2 z^2 S(S+1), \tag{2.10}$$

where a is the lattice constant.

§ 3. Thermal conductivity due to phonons

If we substitute for $\boldsymbol{Q}$ the heat flux operator of phonons,

$$\boldsymbol{Q}^l = \sum_q {}' \omega_q \boldsymbol{v}_q N_q, \quad \boldsymbol{v}_q = \partial \omega_q / \partial \boldsymbol{q}, \tag{3.1}$$

we have for the thermal conductivity due to phonons the following:

$$\kappa^l = \frac{1}{2 V k_B T^2} \sum_q {}' \sum_p {}' \omega_q \omega_p v_q^x v_p^x \int_{-\infty}^{\infty} \langle \{N_q(t), N_p\} \rangle dt, \tag{3.2}$$

where N_q denotes the operator for the number of phonons of mode q[*] which is written as $a_q^* a_q$ with the phonon operators a_q and a_q^* and ω_q the phonon energy spectrum.

In the temporal development of N_q, we shall only retain the diagonal elements of N_q in the number representation, which is equivalent to the kinetic treatment of phonons. Thus we obtain following the same procedure as that used by Mori,[11]

$$\dot{N}_q = - N_q^0 (N_q^0 + 1) \sum_p A_{qp} N_p, \tag{3.3}$$

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[*] q specifies the wave vector as well as the polarization of phonons.

where we introduced the symmetrical matrix A_{qp} defined as

$$A_{qp} = \int_{-\infty}^{\infty} \langle \{\dot{N}_q(t),\ \dot{N}_p\} \rangle dt / 2N_p^0(N_p^0+1) N_q^0(N_q^0+1),\qquad (3\cdot4)$$

N_q^0 being the Planck distribution function of phonons.

Integrating (3·3) formally and substituting the result into (3·2), the thermal conductivity can easily be put into the following familiar form:

$$\kappa^l = \frac{1}{V} \sum_q C_q^{ph}\ v_q^{x2}\ \tau_q,\qquad (3\cdot5)$$

where C_q^{ph} is the phonon specific heat of the mode q defined by

$$C_q^{ph} = \frac{\omega_q^2}{k_B T^2}\ N_q^0(N_q^0+1)\qquad (3\cdot6)$$

and τ_q the relaxation time of the mode q, which satisfies the following equation:

$$\omega_q^2 = \sum_p v^2 A_{qp}\ q\cdot p\ N_p^0(N_q^0+1),\qquad (3\cdot7)$$

v being the sound velocity. In deriving these expressions, we assumed for simplicity that the crystal is isotropic and the phonon spectrum is given by $\omega_q = vq$.

To proceed, we need some knowledge about the spin-phonon coupling. In view of the lack of the precise information about this coupling and in order to avoid too much complications, a simplified macroscopic approach is adopted to determine the effective spin-phonon coupling, restricting ourselves to the case where the magnetic transition temperature T_0 is much smaller than the Debye temperature T_D, namely,

$$T_0 \ll T_D.\qquad (3\cdot8)$$

Under this condition, the wave lengths of most thermal phonons are much longer than the lattice constant, and the effective spin-phonon coupling can be obtained by considering the change of energy of the spin system due to the strain field induced by a phonon in the following manner. Suppose, for example, that the Hamiltonian of the spin system is characterized by a single constant, say, an exchange interaction constant between the nearest neighbor spins J, whose change $\Delta J(r)$ in the presence of a strain $e_{jl}(r)$, then, is expanded as

$$\Delta J(r)/J = \sum_{jl} \alpha_{jl}\ e_{jl}(r) + \sum_{jlmn} \gamma_{jlmn}\ e_{jl}(r)\ e_{mn}(r).\qquad (3\cdot9)$$

$$(j,\ l,\ m,\ n = x,\ y,\ z)$$

The spin Hamiltonian density $H^s(r)$ will then change by the same ratio (3·9). Thus the total change of the spin Hamiltonian, which expresses the effective spin-phonon coupling and is denoted by H', becomes

$$H' = \int H^s(\mathbf{r}) \frac{\Delta J(\mathbf{r})}{J} d\mathbf{r}$$

$$= \sum_{jl} \alpha_{jl} \int e_{jl}(\mathbf{r}) H^s(\mathbf{r}) d\mathbf{r} + \sum_{jlmn} \gamma_{jlmn} \int e_{jl}(\mathbf{r}) e_{mn}(\mathbf{r}) H^s(\mathbf{r}) d\mathbf{r} \cdot \qquad (3\cdot10)$$

Expressing the strain tensors in terms of phonon operators, $(3\cdot10)$ reduces to

$$H' = \sum_q \alpha_q \frac{iq}{\sqrt{2V\rho\omega_q}} [H_q^s a_q - H_q^{s*} a_q^*] + \sum_{q,p} \gamma_{qp} \frac{qp}{2V\rho\sqrt{\omega_q\omega_p}} [H_{p-q}^s a_q^* a_p + H_{q-p}^{s*} a_p^* a_q],$$

$$(3\cdot11)$$

where ρ is the mass density of the lattice and α_q and γ_{qp} are defined as

$$\alpha_q = \frac{1}{2} \sum_{jl} \alpha_{jl} (e_q^j \hat{q}_l + e_q^l \hat{q}_j),$$

$$\gamma_{qp} = \frac{1}{4} \sum_{jlmn} \gamma_{jlmn} (e_q^j \hat{q}_l + e_q^l \hat{q}_j)(e_p^m \hat{p}_n + e_p^n \hat{p}_m), \quad \hat{q}_l = q_l/q$$

where e_q^j is the j-th component of the polarization vector of mode q. In $(3\cdot11)$ we omitted the terms describing the simultaneous emission and absorption of phonons, and in the following we shall assume α_q and γ_{qp} to be constants independent of q and p.

The first term in $(3\cdot11)$ which we shall denote as H_1' describes the emission and the absorption of a phonon in the first order, and the phonon scattering in the second order. The second term describes the phonon scattering, and shall be denoted as H_2'.

In the spin wave region, it is evident from above that the relative change of a magnon energy is independent of the magnon wave number as long as it is much greater than that of phonons. In this sense our effective coupling may be regarded as a generalization of the use of Grüneisen's constant in determining the effective phonon-phonon coupling. A somewhat similar effective coupling was used by Elliott and Stern in their discussion of the width of magnon spectrum.[12]

With this effective spin-phonon interaction, the "kinetic coefficient" A_{qp} can easily be obtained. Corresponding to the emission and absorption (direct processes) and the scattering, A_{qp} can be divided into $A_{qp}^{(1)}$ and $A_{qp}^{(2)}$. Taking account of H_1' up to the first order in $\dot{N}_q(t)$ and $\dot{N}_p$ in $(3\cdot4)$, $A_{qp}^{(1)}$ is obtained as

$$A_{qp}^{(1)} = \delta_{q,p}/N_q^0(N_q^0+1)\tau_q^{(1)}, \qquad (3\cdot12)$$

where

$$\tau_q^{(1)-1} = \frac{\alpha^2 q^2}{4VN_q^0(N_q^0+1)} \int_{-\infty}^{\infty} dt \Big[\exp(-it\omega_q)(N_q^0+1)\langle H_q^s(t)H_q^{s*}\rangle$$

$$+ \exp(it\omega_q)N_q^0 \langle H_q^{s*}(t)H_q^s\rangle \Big] \qquad (3\cdot13)$$

is the relaxation time associated with the direct processes of the mode q. For a small wave number q and in the vicinity of the magnetic transition point, $\langle H_q^s(t) H_q^{s*} \rangle$ is expected to show the same temporal development as the decay of the initial inhomogeneous energy distribution. Thus we can assume

$$\langle H_q^s(t) H_q^{s*} \rangle = \langle H_q^{s*}(t) H_q^s \rangle = \langle H_q^s H_q^{s*} \rangle \exp(-q^2 D^s |t|) \qquad (3 \cdot 14)$$

with the diffusion constant $D^s = \kappa^s / C^s$ discussed in § 2. Noting the relation

$$\langle H_q^s H_q^{s*} \rangle = \langle H_q^{s*} H_q^s \rangle = k_B T^2 V C^s, \quad (q \to 0) \qquad (3 \cdot 15)$$

and using $(3 \cdot 14)$, $(3 \cdot 13)$ becomes

$$\tau_q^{(1)-1} = \frac{\alpha^2 k_B T^2 \kappa^s}{2 \rho v} \cdot \frac{q (C^s/\kappa^s)^2}{q^2 + (v C^s/\kappa^s)^2} \cdot \frac{2 N_q^0 + 1}{N_q^0 (N_q^0 + 1)}. \qquad (3 \cdot 16)$$

Now we turn to the scattering. As we approach the magnetic transition point, the part of the motion of the spin system which is associated with the critical fluctuation slows down as in $(3 \cdot 14)$ where the diffusion constant approaches zero as C^{s-1} (thermodynamic braking[13]). Thus, in order to see the behavior near the transition point, it is legitimate to regard the scattering as wholly elastic.[*] The inelastic part of the scattering, if any, would not show a marked temperature dependence characteristic of the critical fluctuation in the vicinity of the transition point.

There are two contributions to the scattering, the first order term of H_2' and the second order term of H_1'. The latter can be most easily handled by constructing from H_1' the effective Hamiltonian for the scattering which is denoted as H_{11}' as follows:

$$H_{11}' = \sum_{q,p} \frac{\alpha^2 qp}{2 \rho V V \omega_q \omega_p} \left[\frac{H_q^s H_p^{s*}}{-\omega_p} + \frac{H_p^{s*} H_q^s}{\omega_q} \right] a_p^* a_q$$

$$= \sum_{q,p} \frac{\alpha^2 qp}{2 \rho V V \omega_q \omega_p} \frac{[H_p^{s*}, H_q^s]}{\omega_q} a_p^* a_q. \qquad (3 \cdot 17)$$

Here we have neglected the energy change of the spin system considering the slowness of the motion associated with H_q^s, and used that $\omega_q = \omega_p$. The commutator in this expression is written as

$$[H_p^{s*} - H^s, H_q^s - H^s] + [H_p^{s*} - H^s, H^s] + [H^s, H_q^s - H^s].$$

For small wave numbers q and p, the first term of this expression is proportional to qp, the second and the third, to p and q, respectively. Thus if we

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[*] A measure of the inelasticity associated with the scattering due to the critical fluctuation is obtained by considering the average energy transfer between a phonon and the spin system, which, according to $(3 \cdot 14)$, equals $q^2 D^s = q^2 \kappa^s / C^s$. This amounts to the relative change of the phonon energy of the order of $q \kappa^s / v C^s$, which is, for $qv \approx k_B T^0$ and the specific heat of 1 cal. per mol. deg., about 1/20 for CoF_2, and thus is expected to be small over a fairly wide range of temperatures around the transition point.

neglect the term of order pq, the above expression reduces to $i[\dot{H}_q^s - \dot{H}_p^{s*}]$,[*]
and (3·17) becomes

$$H_{11}' = \sum_{q,p} i\alpha^2 \frac{qp}{2V\rho V \omega_q \omega_p} \frac{\dot{H}_q^s - \dot{H}_p^{s*}}{\omega_q} a_p^* a_q. \tag{3·18}$$

In order to compare this with H_2', we estimate the quantity $\langle H_{11}'^2 \rangle / \langle H_2'^2 \rangle$
taken in the high temperature limit, which is from (3·11) and (3·18) roughly
equal to

$$\frac{\alpha^4 (qp)^2 / \omega_q \omega_p \omega_q^2}{\gamma^2 (qp)^2 / \omega_q \omega_p} \cdot \frac{\langle \dot{H}_q^{s2} \rangle_\infty}{\langle H_{q-p}^{s2} \rangle_\infty}$$

for typical q and p of thermal phonons. Using (2·1), (2·6) and (A·5) below,
and noting that $\omega_q = \omega_p$, this reduces for $\alpha^2 \sim \gamma$ to $(bq)^2(zJ/vq)^2/18S^3(S+1)^3$,
which is much smaller than unity when the condition (3·8) is satisfied. Fur-
thermore, in the neighborhood of the transition point, from an argument similar
to that in § 2, the scattering arising from (3·18) is shown to involve no critical
fluctuation. Thus, for our purpose, we may neglect the scattering (3·18).
Substituting $\dot{N}_q = i[H_2', N_q]$ into (3·4), we thus obtain after integration

$$A_{qp}^{(2)} = \frac{2\pi}{N_q^0(N_q^0+1)} \left(\frac{\gamma q}{V\rho v} \right)^2 \{ \delta_{q,p} \sum_r \langle H_{q-r}^s H_{q-r}^{s*} \rangle \delta(\omega_q - \omega_r)$$

$$- \langle H_{q-p}^s H_{q-p}^{s*} \rangle \delta(\omega_q - \omega_p) \}. \tag{3·21}$$

For isotropic crystals and the elastic scattering, the relaxation time τ_p in
(3·7) is independent of the direction of p and equals τ_q, and (3·7) reduces to

$$\tau_q^{-1} = N_q^0(N_q^0+1) \sum_{q,p} A_{pq} \cos \Omega_{qp}, \tag{3·20}$$

where Ω_{qp} is the angle between the vectors q and p.

Corresponding to the two processes $A_{qp}^{(1)}$ and $A_{qp}^{(2)}$, τ_q^{-1} is written as a sum
of $\tau_q^{(1)-1}$ (3·16) and $\tau_q^{(2)-1}$. The latter becomes, using (3·19) and (3·20),

$$\tau_q^{(2)-1} = 2\pi \left(\frac{\gamma q}{V\rho v} \right)^2 \sum_p (1 - \cos \Omega_{qp}) \langle H_{q-p}^s H_{q-p}^{s*} \rangle \delta(\omega_q - \omega_p). \tag{3·21}$$

This is the scattering probability contributing to the thermal resistivity of a
phonon with a wave vector q by the static fluctuations in the energy density
of the spin system. The critical fluctuation reveals itself through $\langle H_{q-p}^s H_{q-p}^{s*} \rangle$.
As will be shown in the Appendix, for small wave numbers this quantity
becomes

$$\langle H_q^s H_q^{s*} \rangle = k_B T^2 V C^s / [1 + (q/q_0)^2], \tag{3·22}$$

where

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[*] This result can also be verified by calculating $[H_p^{s*}, H_q^s]$ directly and taking the limit
$p, q \to 0$.

$$q_0{}^2 = 4k_B nz S(S+1)/[(157/15)S(S+1)-8/5]\cdot 1/C^s a^2. \qquad (3\cdot23)$$

$$(n=N/V)$$

$q_0{}^{-1}$ is a measure of the correlation range of energy density fluctuations in the spin system.

Substitution of $(3\cdot16)$ and $(3\cdot21)$ into $(3\cdot5)$ completes the calculation of the thermal conductivity due to phonons.

§ 4. Behavior near the transition point

As we saw in § 2, the thermal conductivity due to spins κ^s is expected to have only a mild temperature dependence resulting from the short range correlations, and the anomalous temperature dependence at the transition point reveals itself through the magnetic specific heat C^s appearing in $(3\cdot16)$, $(3\cdot22)$ and $(3\cdot23)$.

We first consider the direct process $(3\cdot16)$. The factor involving C^s there is $1/[1+(q\kappa^s/vC^s)^2]$. Use of $(2\cdot5)$ and $(A\cdot5)$ below yields for a typical thermal phonon at the transition temperature with the wave vector $q=k_B T_0/v$,

$$q\kappa^s/vC^s = 9\tau (k_B T_0)^3/48nv^2aS(S+1)\cdot (T^2 C^s)_{T=\infty}/T^2 C^s.$$

From $(2\cdot7)$ we see that $\tau\sim 1/J$, and if we note $v^2 na\sim (v/a)^2\sim (k_B T_D)^2$ the factor multiplying $(T^2 C^s)_{T=\infty}/T^2 C^s$ in the above expression comes to be of the order of $(T_0/T_D)^2$ which is much smaller than unity under the condition $(3\cdot8)$. Thus, the increase of the thermal resistivity in the vicinity of the transition point due to the direct processes which is proportional to $\tau_q^{(1)-1}$ is rather insignificant. This situation is the result of a near cancellation of the two competing effects. From $(3\cdot11)$, the square of the matrix element for this process is proportional to $\langle H_q{}^s H_q{}^{s*}\rangle$, or to C^s for small q. On the other hand, the energy emitted or absorbed on annihilating or creating a phonon must be absorbed by or taken away from the spin system. This probability is, by $(3\cdot14)$, proportional to

$$\int_{-\infty}^{\infty} \exp(-q^2 D^s|t|)\exp(\pm i\omega_q t)\,dt,$$

and hence to $2q^2(\kappa^s/C^s)/\{(q^2\kappa^s/C^s)^2+\omega_q{}^2\}$, or to $1/C^s$ for very large C^s in the vicinity of the transition point. This reduction of the probability is another manifestation of the thermodynamic braking which is discussed in the paragraph preceding $(3\cdot17)$.

Now we are left with the relaxation time associated with the scattering which, substituting $(3\cdot22)$ into $(3\cdot21)$ and carrying out the summation over p, becomes

$$\tau_q^{(2)-1} = \gamma^2 k_B T^2 C^s q^4 / 2\pi \rho^2 v^3 \cdot F(q^2/q_0^2) , \tag{4.1}$$

where

$$F(x) = \frac{1}{x}\left\{1 - \frac{1}{4x}\ln(1+x)\right\} = \left\{\begin{array}{l} 2 - 16/3x + \cdots (x \ll 1) \\ 1/x - \ln x/4x^2 + \cdots (x \gg 1) \end{array}\right. . \tag{4.2}$$

The qualitative behavior of the thermal resistivity due to the scattering near the transition point is immediately clear from the above results. When we are not too close to the transition point and $q \ll q_0$, that is, when the correlation range of energy density fluctuation is small compared to the phonon wave length, $\tau_q^{(2)-1}$ is proportional to q^4 (Rayleigh scattering) and increases as C^s when the transition point is approached. At the same time, however, the correlation range increases as C^s, and when this exceeds the phonon wave length, the factor $F(q^2/q_0^2)$ reduces the rate of increase of the resistivity, and at the transition point, $\tau_q^{(2)-1}$ reaches a finite limit:

$$\tau_q^{(2)-1} = 2n(k_B T_0)^2 \gamma^2 / \pi \rho^2 v^3 a^2 \cdot zS(S+1) / [(157/15)S(S+1) - 8/5] \cdot q^2 . \tag{4.3}$$

This is due to the situation that as the correlation range becomes much greater than the phonon wave lengh, the small angle scattering predominates, which tends to reduce the thermal resistivity.

As a numerical example, we consider the case of CoF_2, where we use the following set of parameters:

$$\left.\begin{array}{lll} T_0 = 37.7^\circ K, & a = 4\text{Å}, & v = 3 \times 10^5 \text{cm/sec} \\ T_D = 500^\circ K, & z = 8 \text{(b.c.c.)}, & S = 1/2 \\ \rho = 4.6 \text{ gr./cm}^3, & n = 2/a^3, & b = \sqrt{3}/2 \cdot a \end{array}\right\} . \tag{4.4}$$

Then, assuming (2.9) and using the results of this and the preceding sections, the thermal conductivity due to the spin system κ^s and the mean free paths $l^{(i)} = v\tau_q^{(i)}$ ($i = 1, 2$) of a typical thermal phonon with $q = k_B T/v$ associated with the direct and the scattering processes in the neighborhood of the transition point are obtained as follows:

$$\left.\begin{array}{l} \kappa^s = 0.9 \times 10^{-4} \text{ watts/cm deg} \\ l^{(1)}(T)^{-1} = 0.27 \times \alpha^2 / [1 + (1/40C^s)^2] \times 10^{-7}\text{Å}^{-1} \\ l^{(2)}(T)^{-1} = 1.2 \times 10^{-19} \times \gamma^2 T^6 C^s F(4 \times 10^{-4} T^2 C^s)\text{Å}^{-1} \end{array}\right\} , \tag{4.5}$$

where C^s is expressed in cal/mol deg.

The observed thermal conductivity of CoF_2 in the temperature range of interest is of the order of 1/10 watts/cm deg,[2] and κ^s is negligible. Slack[2] deduced from his experiment on CoF_2 that the phonon mean free path due to the spin-phonon interaction is about 2200 Å above the transition point. If we tentatively suppose that the main contribution to the thermal resistivity
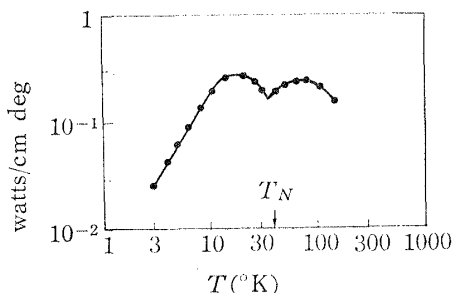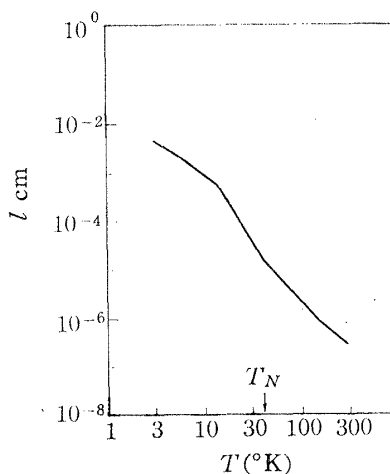
Fig. 1. Observed thermal conductivity of CoF_2.[2]

Fig. 2. Phonon mean free path deduced from thermal conductivity.[2]

due to the spin-phonon coupling comes from the scattering, and equate this mean free path to $l^{(2)}(T)$ at the transition point where C^s is assumed to be infinite, it follows that the value of the order of 10^3 for γ is required.

At this moment, only a little is known about the spin-phonon coupling in CoF_2 crystals, therefore, only an order of magnitude argument will be given here. Very recently, Sinha and Upadhyaya[14] studied the spin-phonon coupling induced by the transition of the ground orbital state to the excited electronic states by the strain due to phonons. If we write the matrix elements of the transition schematically as $f \cdot e + g \cdot e^2$, where e denotes a component of the strain tensor and f and g involve the first and the second derivatives of the crystalline field with respect to the ionic displacement, their results amount for our α and γ roughly to the following:

$$\alpha \sim f/\varDelta, \quad \gamma \sim (f/\varDelta)^2 + g/\varDelta, \tag{4·6}$$

where $\varDelta$ is the energy separation between the ground and the excited states. If $f \gg \varDelta$, we would have $\gamma \sim \alpha^2$. Therefore, if the above argument applies to CoF_2, the value of 10^3 for γ leads to the value of about 30 for $|\alpha|$, which may not be unreasonable. See the end of this section. With this value of $|\alpha|$, $l^{(1)}(T)$ becomes about 4×10^4 Å, and is greater than $l^{(2)}(T)$. Thus we conclude that the main qualitative feature of the thermal conductivity in the vicinity of the transition point arises from the critical scattering of thermal phonons by the critical fluctuations of the energy density of the spin system. Using the measured values of C^s of Stout and Catalano with the correction of the lattice specific heat,[15] we have plotted $l^{(2)}(T)$ in Fig. 3. In Figs. 1 and 2 we reproduced the observed thermal conductivity and the phonon mean free path.[2] The phonon mean free path l here is deduced from the thermal conductivity of Fig. 1 by using the formula,
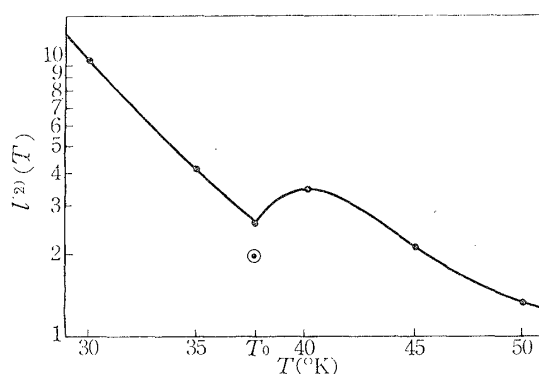
Fig. 3. Phonon mean free path for scattering vs. temperature. The ordinate is in arbitrary units. Dots are calculated values using the measured values of the specific heat of Stout and Catalano.[15] ⊙ is a value when C^s is assumed to be infinite at the transition point.

$$\kappa = \frac{1}{3} l v C_{ph},$$

where C_{ph} is the lattice specific heat. It is seen that our result of Fig. 3 qualitatively agrees with the experiment. For a more complete treatment other types of phonon scattering than that arising from spin-phonon coupling must be taken into account. We must also consider the situation in which the magnetic properties of CoF_2 are not well described by a simple Heisenberg Hamiltonian because of the remaining orbital angular momenta and the existence of the low-lying excited orbital states.[16]

Finally it is of some interest to study the case of MnF_2, particularly because the magnitude of the effective spin-phonon coupling can be estimated from the NMR experiment under pressure for this crystal.[17][*] Let us suppose that a pressure P is applied to the crystal. (3·9) then gives

$$\frac{1}{J}\left(\frac{\partial J}{\partial P}\right)_T P = \alpha (e_{xx} + e_{yy} + e_{zz}) = \alpha \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T P, \qquad (4\cdot7)$$

where we omitted the second term of (3·9) and assumed $\alpha_{xx} = \alpha_{yy} = \alpha_{zz} = \alpha$. We also neglected the off diagonal parts of the strain tensor. If we assume that the exchange integral J is proportional to the Neél temperature, we have $(\partial J/\partial P)_T/J = (\partial T_N/\partial P)_T/T_N$. Expressing the compressibility in (4·7) in terms of the fractional change of the lattice constants a and c in the direction of a- and c-axes, (4·7) reduces to

$$\left(\frac{\partial \ln T_N}{\partial P}\right)_T = \alpha\left(2\frac{\partial a/\partial P}{a} + \frac{\partial c/\partial P}{c}\right). \qquad (4\cdot8)$$

Fractional changes of T_N, a, and c under pressure have been measured by Benedek and Kushida,[17] and substitution of their results into (4·8) yields $\alpha = -3.6$.

On the other hand, α can also be deduced from the thermal conductivity as for CoF_2. According to Slack,[2] the phonon mean free path above T_N due to spin-phonon interaction is 4000 Å. In the same manner as was done for CoF_2, we obtained $|\alpha| = 8$ for MnF_2, where we have taken $\rho = 4gr./cm^3$, $T_0 = T_N = 68°K$ and $S = 5/2$, other parameters being the same as for CoF_2. This value is about twice that deduced from the NMR experiment. For a more quantitative discus-

[*] The author is grateful to the referee for bringing up this reference to author's attention.

sion, we would have to consider a more realistic spin-phonon coupling for this crystal.

§ 5. Conclusion and some remarks

In the preceding sections we studied the thermal conductivity in magnetic insulating crystals near the magnetic transition point. The thermal conductivity due to the spin system is shown to be negligible near and above the transition point, although it may become observable in the low temperature region. In considering the thermal conductivity due to phonons, the direct processes and the scattering have been studied when the magnetic transition temperature is much smaller than the Debye temperature. The direct processes turned out to have little influence on the temperature dependence at the transition point. The anomaly of the thermal conductivity at the transition point is interpreted as the critical scattering of phonons due to the critical fluctuation of the spin energy density which appears through the specific heat.

Here arises the question whether the conclusions obtained depend on the specific choice of the spin-phonon coupling we have made, and what happens if the condition (3·8) no longer holds. In order to answer the first question, let us consider the following spin-phonon interaction of a more general type:

$$H' = \sum_q \frac{iq}{\sqrt{2\rho V \omega_q}} [\varphi_q a_q - \varphi_q^* a_q^*] + \sum_{q,p} \frac{qp}{\rho V \sqrt{\omega_q \omega_p}} \psi_{qp} a_q^* a_p, \qquad (5·1)$$

where φ_q and ψ_{qp} are any operators involving spins, in which we left out the parts which do not involve critical fluctuations, because the resistivity arising from them would not show the temperature dependences of our interest.

First consider the case where φ_q and ψ_{qp} reduce to the constants of motion for vanishing q and p, such as the total Hamiltonian and the total magnetization. Then the same analysis as in the preceding sections shows that under the condition (3·8), the phonon relaxation time associated with the direct processes will be given by (3·16) where C^s is replaced by the quantity proportional to $\lim_{q \to 0}\langle \varphi_q^* \varphi_q \rangle$, and its temperature dependence would again be insignificant. The phonon relaxation time associated with the scattering will similarly be given by (4·1) and (3·23) where C^s is replaced by the quantity proportional to $\lim_{qp \to 0}\langle \psi_{qp} \psi_{qp}^* \rangle$. Thus the behavior of the thermal conductivity near the transition point will again be characterized by the critical scattering of phonons which in this case, however, is described by $\lim_{qp \to 0}\langle \psi_{qp} \psi_{qp}^* \rangle$ instead of C^s.

If, on the other hand, the parts of φ_q and ψ_{qp} which do not reduce to the constants of motion for vanishing q and p are important, the above conclusions would have to be somewhat modified. A similar analysis may be made and the phonon relaxation rate associated with the direct processes would have a

pronounced finite peak at the transition point in contrast with the preceding results. The analysis which led us to discard H_{11}' in §3 cannot be applied here. However, if we ignore this complication, the behavior of the phonon relaxation time associated with the scattering is the same as in the preceding paragraph.

Concerning the second question, our analysis which is based on the macroscopic treatment of the spin system breaks down once the magnetic transition point becomes comparable to the Debye temperature even with our choice of the simple spin-phonon coupling, because here we have to deal with the short range space-time correlations of spins in the vicinity of the transition point for which no reliable treatment is possible at present. In this case, the direct processes as well as the scattering would be important for understanding the behavior of the thermal conductivity near the transition point.

Appendix

The static pair correlation of the Hamiltonian density operator

In discussing the thermal conductivity due to phonons, we encountered with the quantity $\langle H_q^s H_q^{s*} \rangle$, which involves the correlation of four spin operators and cannot be calculated in a simple way with the known approximation schemes. Nevertheless, the following simple procedure yields an expression for this quantity which seems reasonable.

First note that this quantity reduces to $k_B T^2 V C^s$ for vanishing q, which becomes very large near the transition point due to the critical fluctuation of the energy density. Thus if one supposes that the usual theories of critical fluctuations[18,19] are applicable here, $\langle H_q^s H_q^{s*} \rangle$ has the following form for small q :

$$\langle H_q^s H_q^{s*} \rangle = k_B T^2 V C^s / [1 + (q/q_0)^2], \qquad (A \cdot 1)$$

where q_0 gives the inverse of the correlation range of fluctuations, and is an analogue of Van Hove's parameter κ_1 for the static pair correlation of spins.[18] In the vicinity of the transition point, the correlation range of fluctuations becomes very large according as

$$q_0^2 = \zeta / C^s, \qquad (A \cdot 2)$$

where ζ is approximately independent of temperature. Substituting (A·2) into (A·1), we obtain

$$\frac{1}{\zeta} = \frac{1}{VC^s q^2} \left[\frac{k_B T^2 VC^s}{\langle H_q^s H_q^{s*} \rangle} - 1 \right].$$
(A·3)

We neglect the temperature dependence of the above expression, and evaluate it in the high temperature limit.

At very high temperatures and for small q, we have

$$\langle H_q^s H_q^{s*} \rangle = \langle H^{s2} \rangle_\infty \left\{ 1 - \frac{S(S+1)}{2} \left(\frac{J}{k_B T} \right)^2 \left[\frac{157}{45} S(S+1) - \frac{8}{15} \right] (aq)^2 + \cdots \right\},$$
(A·4)

where

$$\langle H^{s2} \rangle_\infty = \frac{48N}{9} [JS(S+1)]^2 = [k_B T^2 VC^s]_{T=\infty}.$$
(A·5)

Substituting these results into (A·5), we see that it reduces to a finite value in the limit $T \to \infty$ and $q \to 0$, and yields

$$\zeta^{-1} = \frac{3a^2}{4z k_B n S(S+1)} \left[\frac{157}{45} S(S+1) - \frac{8}{15} \right].$$
(A·6)

This together with (A·2) leads to (3·23).

In order to test the above procedure, we applied it for the evaluation of the spin pair correlation function $\langle S_q^z S_q^{z*} \rangle$ above the Curie point, where S_q^z denotes the Fourier component of the spin density operator. In accordance with the fluctuation theory, we assumed

$$\langle S_q^z S_q^{z*} \rangle = \frac{N k_B T \chi}{(g\mu_B)^2} \Big/ [1 + (q/\kappa_1)^2], \quad (\chi: \text{the susceptibility per atom})$$

and setting $\kappa_1^2 = \xi/\chi$, we determined ξ in the high temperature limit with the result $1/\xi = 2Ja^2/(g\mu_B)^2$, which agrees with that obtained by other methods.[9],[13],[20]

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