Critical Phonon Scattering near a Ferromagnetic Transition and Its Effect on the Thermal Conductivity of $CuK_2Cl_4 \cdot 2H_2O$

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By comparing the thermal conductivity in a magnetic field large enough to align the spin system with the conductivity at zero field, it has been possible to measure the change in the thermal conductivity due to critical scattering near the transition in the cubic Heisenberg ferromagnet $CuK_2Cl_4 \cdot 2H_2O$. A phonon scattering law deduced from these results agrees well with ultrasonic attenuation measurements on the ferromagnet gadolinium. Some comparison has been possible between these results and dynamical scaling laws in their present form.

IN this paper, we present measurements of the change in thermal conductivity due to scattering from critical fluctuations near a magnetic transition. These results were obtained on single crystals of $CuK_2Cl_4 \cdot 2H_2O$, which, below 0.88°K,[1] becomes very nearly an isotropic, Heisenberg ferromagnet. From these results we have been able to deduce the temperature dependence of the scattering cross section for phonons by the critical fluctuations.

Often the presence of magneto-elastic coupled modes has an important effect on the conductivity.[2–4] Interactions between the lattice and the spin system, present both above and below the transition temperature, result in coupled magneto-elastic modes which result in diminished conductivity. The effect of these modes is weak for this double salt, and could not be detected. This implies that the only effect of the magnetic system on the phonons is the scattering by fluctuations in the magnetic order near the Curie temperature. Since this temperature is relative low, it should be possible to eliminate the interaction altogether by applying a strong enough magnetic field to superimpose a ferromagnetic order on the magnetic system. The difference between the high-field and zero-field conductivity should be entirely due to phonon scattering by the critical fluctuations.

The experiments were performed on single crystals of $CuK_2Cl_4 \cdot 2H_2O$ grown from aqueous solution. A thermal-conductivity sample 4.0×0.5×0.3 cm was cut with a string saw oriented so that the long direction was inclined about 6° to the [101] axis. The thermal conductivities were measured by the conventional potentiometric technique, and a magnetic field parallel to the heat-flow direction was provided by a 45-kOe superconducting magnet.

Representative results for the change in thermal conductivity with magnetic field, both above and below the transition temperature, are shown in Fig. 1. The thermal conductivity as a function of temperature is displayed by the results shown in Fig. 2, both at a sufficiently high field to saturate the magnetic system and at zero field. At the highest temperatures, however,

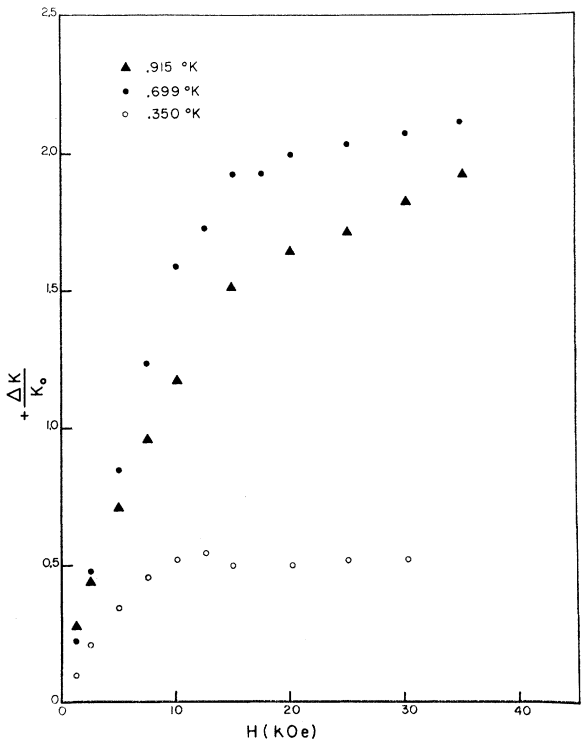

FIG. 1. Change in thermal conductivity with magnetic field.

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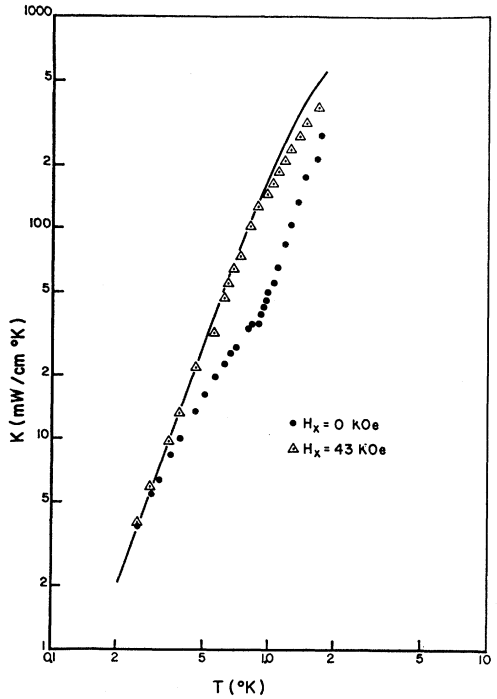

FIG. 2. Change in thermal conductivity with temperature.

the field was not quite large enough to saturate the system completely.

Reference to Fig. 1 reveals that the conductivity is a monotonically increasing function of the magnetic field. This was true at all temperatures in the range 0.25°K $<T<2$°K. Had there been any important effect of the magneto-elastic modes on the thermal conducitvity, this would have resulted in an initial decrease in conductivity with increasing field. The reason is the following: The coupled modes in effect restrict the contribution to the heat current of carriers whose frequency is close to the Larmor frequency of the spin system in the paramagnetic phase,[4] or whose frequency is such that the magnon and phonon frequencies are equal for equal wave vector in the ordered phase.[2,3] The strength of the interaction determines the range of frequencies affected. In a magnetic field the Larmor frequency is raised, and the magnon energies are raised; thus the frequencies of the affected carriers is increased. Since the contribution of the heat carriers is peaked about an energy of the order of $4kT$, the application of a magnetic field initially suppresses the contribution of more important carriers, and the conductivity should decrease initially, and then recover. A diligent search revealed no such initial decrease, and we must conclude that the effect of this kind of interaction is negligible in our crystals. Thus, to a good approximation, all the phonon scattering by the magnetic system appears to be due to the critical fluctuations.

Thus we may conclude that although the spin-phonon coupling is not strong enough to lead to a large effect from the magneto-elastic modes at temperatures far from T_C, the critical scattering is still appreciable. This is not necessarily inconsistent, although the same spin-phonon coupling mechanism can lead to both effects: The magneto-elastic modes are confined to a narrow range of frequencies, but the critical scattering affects all phonon frequencies.

It is interesting to attempt to infer a critical scattering law from the data. We have done this in effect by assuming that the high-field results represent the intrinsic phonon conductivity and then finding out what scattering function, when included in the expression which reproduces the high-field results for the conductivity, will reproduce the zero-field results. A more accurate fit is obtained, however, if the difference in conductivities is used. Thus, the phonon scattering function will be inferred by fitting K_H-K_0 as a function of T. It is necessary, first, to determine the intrinsic scattering function for the crystal. This was done in the conventional manner by fitting the results at 43 kOe to the expression

$$K(T)=AT^3\int_0^\infty \frac{x^4e^x dx}{(e^x-1)^2(1+Bx^4T^4)}. \qquad (1)$$

We have, in effect, assumed that the conductivity is limited only by the boundaries and scattering by point defects (normal processes may be safely neglected at these temperatures). With $A=0.25\times10^{-2}$ W/cm² °K and $B=0.0005$(°K)$^{-4}$, the straight line which passes through the high-field points shown in Fig. 2 was obtained. The value of B was chosen so that the calculated curve would lie above the measured values of K at the higher temperatures, since the conductivity was still increasing slightly with magnetic field at these temperatures. In any case, the fit to ΔK is relatively insensitive to the choice of B. Next a relaxation time due to critical scattering was included in the denominator of Eq. (1).

In general, the phonon damping due to critical fluctuations is expected to be proportional to $\omega^2/(T-T_C)^p$.[5] The theory does not apply close to the transition temperature, and the damping has been observed to remain finite.[6] Therefore, the phonon relaxation time included in this way was taken as $\tau^{-1}=D\omega^2/(T-T_C)^p+C$. The parameter C is strictly phenomenological, and has the effect of limiting the cross section at $T=T_C$ but preserves the frequency dependence: Lüthi and Pollina's[6] results indicate that the ultrasonic attenuation is still frequency-dependent at T_C. Halperin and Hohenberg[7] have noted that the spin diffusion constant for a fixed wave vector $\mathbf{k}$ becomes temperature-insensitive for k^{-1} less than the range of the two-spin correlation function. Thus, our parameter C is probably related to the temperature at which $k\xi^{-1}\approx1$, where ξ is the correlation length.

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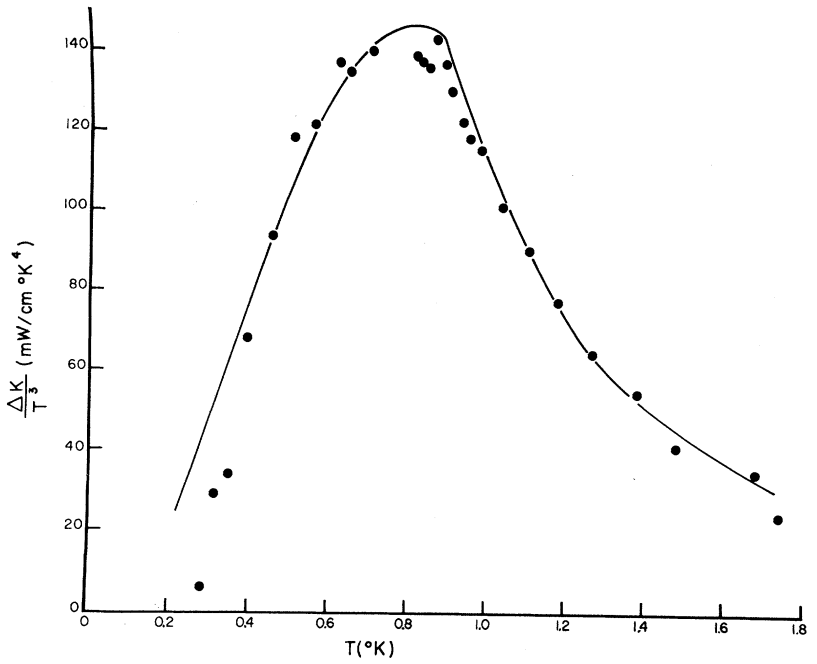

FIG. 3. Change in $\Delta K = K_H - K_0$ with temperature.

The conductivity now is given by

$$K(T) = 9.25\times10^{-2}T^3 \int_0^\infty \frac{x^4 e^x dx}{(e^x-1)^2\{1+5\times10^{-4}x^4T^4+Dx^2T^2/[(T-T_C)^p+C]\}}, \tag{2}$$

where the same form of magnetic scattering has been assumed for all three polarizations. Equation (1) was subtracted from (2) and a fit to the data was attempted by varying D, p, and C.

Thermal conductivities are typically accurate to better than 5%; so agreement to at least 10% was desired. The result of fitting the data is shown as the solid line in Fig. 3. It should be noted that the ratio D/C determines the magnitude of $\Delta K(T_C)$, and consistency requires that this ratio be the same in both temperature ranges.

There is no *a priori* requirement that the scattering cross section for a phonon from a disordered region in a largely ordered matrix be equal to that from an ordered region of equal size in a disordered matrix; so D can be expected to be different above and below T_C. Above the Curie temperature, a separate determination of both D and p was possible with the result that $p=1.3\pm0.2$ and $D=0.025\pm0.005$. The remaining parameter, C, is, of course, determined by the requirement that the scattering remain finite at T_C. The solid line shown in Fig. 2, then, is a plot of the change in conductivity with the choice $D=0.025$, $C=0.067$, and $p=1.3$ above T_C. Below T_C we were unable to obtain a reliable value for the exponent p, since the fit was adequate for $1.0<p<3.0$. The solid line shown is for $p=2.0$, $D=0.06$; however, these values should be viewed with caution.

Our value for the exponent of $T-T_C$ above T_C agrees with Lüthi's results. It is interesting that there does not appear to be a large difference between an insulating and conducting ferromagnet in this respect. If our value for C does in fact scale as $k\xi^{-1}$, it is interesting to compare this with the results on gadolinium. Our choice of $C=0.067$ implies that $k\xi^{-1}\sim1$ for $T-T_C\sim0.067$°K or $T/T_C-1\sim10^{-1}$. If we assume that the independence of the attenuation close to T_C which Lüthi and Pollina have observed is not due to impurities as they have suggested, but is due to $k\xi^{-1}$ becoming less than 1, their attenuation becomes temperature-independent at $T/T_C-1\sim10^{-3}$. Phonon frequencies corresponding to 1°K are of the order of 10^{10} Hz, whereas Lüthi and Pollina's experiments were conducted in the neighborhood of 10^8 Hz. Thus our results and those on gadolinium appear to be consistent with Halperin and Hohenberg's suggestion.

According to Stern[8] and Kawasaki,[9] the ω^2 contribution to the damping should be proportional to the magnon thermal conductivity K_s, all other potentially singular factors cancelling out. The prediction[5] and observation[6] of a large ω^2 term in ultrasonic attenuation measurements has led to the suggestion[10] that K_s may become large near T_C. Experimentally, such a circumstance would have an effect similar to that expected of the magneto-elastic modes: The thermal conductivity as a function of field should show an initial

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decrease with increasing field. This is due to the increased energy and resultant reduction in the number of available magnon states and in their group velocity. Such behavior was not observed in the range of these measurements.

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Light Scattering from Phonons and Magnons in $RbNiF_3$

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The spectrum of inelastically scattered laser light from $RbNiF_3$ is investigated as a function of temperature between 10 and 300°K and of magnetic field between 0 and 50 kOe. $RbNiF_3$ crystallizes in a structure isomorphic to the hexagonal modification of $BaTiO_3$, space group D_{6h}^{14}. Since there are six formula units per unit cell, there are 90 phonon modes, of which 33 are predicted to be Raman-active. Of these we have observed and identified 27 Raman-active phonons. Below 139°K, $RbNiF_3$ becomes ferrimagnetic. We have observed light scattering from a two-magnon excitation of net spin zero. The identification of this feature is based on the temperature and magnetic field dependence of its frequency and width, which are presented in detail. The behavior of the magnetic scattering, which persists above the transition temperature, is discussed in relation to earlier magnon sideband experiments.

I. INTRODUCTION

CONSIDERABLE interest has arisen lately in the magnetic[1,2] and optical[3–5] properties of $RbNiF_3$. The crystal structure[6] is isomorphic to the hexagonal modification of $BaTiO_3$, space group D_{6h}^{14} ($P6_3/mmc$), which has six formula units per unit cell. Below 139°K $=T_c$, $RbNiF_3$ becomes magnetically ordered,[2,3] exhibiting a spontaneous moment in the basal plane. Magnetic susceptibility measurements,[2,3] as well as recent magnetic resonance experiments[1] indicate that below T_c, $RbNiF_3$ may be regarded as a simple colinear *ferrimagnet* wherein the expected saturation magnetization is $\frac{2}{3}M_{Ni}$, resulting from two A-site Ni^{++} ions whose spins align antiparallel to four B-site Ni^{++} ions (see Fig. 1). Optical absorption and the Faraday rotation[3,5] in $RbNiF_3$ have been studied between 0.5 and 2.5×10^4 cm^{-1} and results are also found to be consistent with the above picture.

Although the spin-wave spectrum of $RbNiF_3$ should be rather complicated, owing to the presence of six magnetic ions per unit cell, experimental results to date on this question are rather sparse. Zanmarchi and Bongers[5] have identified some features in the optical-absorption spectrum (of the $3A_2\rightarrow{}^1E^a$ transition) as magnon sidebands, but their infrared (IR) spectra ($\gtrsim 500$ cm^{-1}) showed no evidence of direct absorption by either one- or two-magnon processes. However, several of the IR features and optical absorption structure were attributed to phonons. No measurements of the Raman-active phonons have been reported prior to this work.

In this paper we extend and complement previous work on phonons and magnons in $RbNiF_3$ by a study of its Raman spectrum at temperatures between 10 and 300°K and in magnetic fields of up to 50 kOe. We present here the frequencies and symmetries of 27 of the 33 group theoretically predicted Raman-active phonons together with a semiquantitative explanation of the observed scattering of magnetic origin.

The most striking observation in our experiments is a rather broad peak in the scattered spectrum, whose frequency and linewidth behavior with temperature and magnetic field suggest that it arises from pairs of zone-boundary magnons excited on opposite (A and B) sublattices. Though considerably broader and weaker

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