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Thermal conductivity of antiferromagnetic $RbMnF_3$†

J. B. Hartmann*
Cornell University, Ithaca, New York 14850
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The thermal conductivity of pure and doped $RbMnF_3$ crystals was measured to look for a magnon contribution to the heat conduction and to determine the effect of impurities on the magnetic-field-dependent conductivity. Multiple growing yielded crystals with thermal conductivities at least 35% higher than the phonon boundary scattering limit for $100 < T < 180$ mK. The effect of a 5.5-kG magnetic field was measured between 0.3 and 2.5 K for singly and doubly grown samples and for samples doped with Fe, Ni, or Co. A variety of field effects was observed, indicating magnetic impurities must be carefully considered in the interpretation of field-dependent data. Two of the highest conductivity samples were measured in a 20-kG field for $100 < T < 400$ mK. The field dependence of one agreed qualitatively with predicted spin-wave behavior, but the second did not give the same results. Thus, the magnetic-field effects were probably caused by impurities, even though these samples had a higher thermal conductivity relative to the Casimir limit than any previously reported for magnetic materials.

I. INTRODUCTION

Thermal conductivity measurements have provided valuable information about phonon interactions in dielectric crystals. Phonons may scatter from the sample boundaries, dislocations, point defects, and other impurities or imperfections in the crystal. As a result of systematic studies of crystals with known defect concentrations, these phonon processes are basically well understood.

In magnetic materials, the spin waves may also scatter phonons. Alternatively, however, they may enhance the thermal conductivity by providing additional modes for heat transport. There have been several reports of either spin-phonon scattering or enhanced thermal conductivity in magnetic materials.[1-11] However, these studies were made on poorly characterized crystals. The low-temperature thermal conductivity was often a factor of 10 and even 1000 times lower than would be expected for boundary-scattered phonons. This contrasts with nonmagnetic dielectrics where the understanding of phonon processes has been gained by measuring crystals with phonon mean free paths equal to the sample size at low temperatures and then systematically varying the defect concentration.

Without better quality magnetic crystals and a study of impurity effects in these materials, interpretation of the thermal conductivity in terms of intrinsic spin-wave processes is questionable. For example, Slack concludes that the reported spin-wave contributions to the thermal conductivity of $Y_3Fe_5O_{12}$ may well be impurity effects.[12] Also, our measurements of MnF_2 indicate that an increase in thermal conductivity seen by Stutius and Dillinger[13] and attributed to magnons is probably just a recovery from a broad OH^- resonance.[14]

$RbMnF_3$ is a nearly ideal Heisenberg antiferromagnet.[15] Its low magnetic and crystalline anisotropy and high Néel temperature make it an attractive material in which to look for a spin-wave thermal conductivity. In the experiments to be described here, the thermal conductivity of pure and of doped $RbMnF_3$ crystals was studied in both zero and applied magnetic field in an effort to separate intrinsic spin-wave from magnetic impurity effects.

II. THEORY

In nonmagnetic materials of high purity and perfection, the thermal resistance at temperatures well below the Debye temperature for the solid is produced by phonon scattering from sample boundaries. The thermal conductivity in the Casimir boundary scattering limit is given by

$$K(T)=\tfrac{2}{15}\pi^2 k(kT/\hbar)^3\langle v^{-2}\rangle l\,, \tag{1}$$

where the effective phonon mean free path l is $1.12d$ for a sample of square cross section with width d, and $\langle v^{-2}\rangle$ is the average over all directions of the inverse square of the phonon phase velocity.[16] The other symbols have their usual meaning.

With the elastic constant data for $RbMnF_3$, the quantity $\langle v^{-2}\rangle$ was computed using over 200 different crystallographic directions.[17,18] The result was $\langle v^{-2}\rangle = (3.57\times 10^5\ \mathrm{cm/sec})^{-2}$. The phonon thermal conductivity in the boundary scattering limit is then $K = 0.358dT^3\ \mathrm{W\,cm^{-1}\,K^{-1}}$ for $RbMnF_3$, where d is the sample width. This value is about 18% higher than would be calculated from the Houston approximation[19] for $\langle v^{-2}\rangle$.

The Casimir value is an approximation to the thermal conductivity. Other factors such as specular reflection, end effects, and phonon focusing may change it somewhat. McCurdy, Maris, and

Elbaum have calculated the thermal conductivity for several materials taking into consideration phonon focusing.[20] For crystals with anisotropy similar to $RbMnF_3$, the conductivity is decreased from the Casimir limit by about 10% for heat flow along a ⟨100⟩ axis in a sample with {100} side faces and of infinite length. A finite length correction further reduces the conductivity. Thus, although the phonon focusing and finite length corrections have not been made for $RbMnF_3$, it is probable the corrected theoretical thermal conductivity would be (10–15)% lower than the Casimir value.

In magnetic materials, the spin waves may also contribute to the thermal conductivity. The solid line in Fig. 1 shows the spin-wave dispersion curve in zero magnetic field for $RbMnF_3$.[15,21] In zero field, the two antiferromagnetic spin-wave modes are degenerate. The curve shown is for the ⟨100⟩ direction; however, the orientational dependence is negligible for wave numbers up to about 2×10^{-1} Å^{-1}. There is a finite excitation energy for magnons at zero wave number because of the magnetic anisotropy energy. However, for wave numbers in the range 5×10^{-3}–2×10^{-1} Å^{-1}, the dispersion relation is linear (as in the phonon case), and we find a magnon velocity $v_m = 3.18\times10^5$ cm/sec.

The spin-wave energy gap corresponds to a temperature of 0.37 K. For $T > 0.37$ K, the magnon contribution to the thermal conductivity can be approximated by Eq. (1) modified by a factor $\frac{2}{3}$ to account for two spin-wave modes versus three for phonons. Using the v_m given above, the result is $K_m = 0.27 l_m T^3$ W cm^{-1} K^{-1}, where l_m is the magnon mean free path. Thus, if their mean free paths are comparable, the magnon and phonon thermal conductivities are the same order of magnitude.

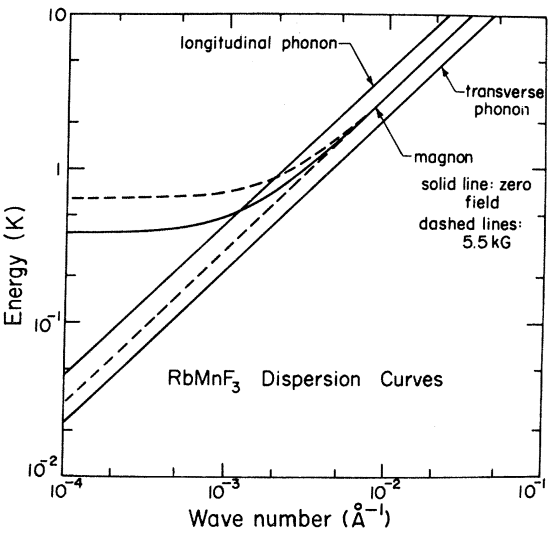

FIG. 1. Dispersion curves for $RbMnF_3$. The phonon lines were calculated from elastic constant data, Ref. 17; the magnon lines from neutron scattering and antiferromagnetic resonance data and from spin-wave theory, Refs. 15, 21, and 24.

At very low temperatures, because of the anisotropy gap, the spin-wave density of states and, hence, the thermal conductivity will decrease exponentially. A numerical approximation to the magnon thermal conductivity was made and showed a noticeable decrease from the above T^3-dependent value at temperatures around 100–130 mK. At lower temperatures, only phonons would be important.

The thermal conductivity of a magnetic material may be depressed because of spin-phonon scattering. Direct coupling between spin and lattice waves will perturb the dispersion relations, particularly in the region where the magnon and phonon branches cross. This has been considered for the ferromagnetic case by Kittel,[22] who found the phonons to be highly damped close to the crossover point of the spin-wave and phonon dispersion curves and to be essentially unchanged far from resonance. In a dominant phonon approximation, the temperature at which this type of scattering should occur in $RbMnF_3$ is around 180 mK.

Two-magnon–one-phonon scattering processes may also be important in some systems. Transition probabilities for these processes have been derived for antiferromagnets and applied to a calculation of thermal conductivity.[23] The relaxation frequency of a phonon of wave number q was found to be proportional to Tq^4 for scattering by spin waves. In these calculations, the magnons were assumed to have very short lifetimes, and the effects of the anisotropy gap were ignored. The number of magnons drops off exponentially at low temperature because of the anisotropy gap. With the decline in number of magnons, the scattering would decrease and the conductivity recover to the phonon boundary scattering limit.

In materials for which this spin-phonon scattering process is important, the thermal conductivity may increase when a magnetic field is applied. A magnetic field lifts the degeneracy of the antiferromagnetic spin-wave modes as shown by the dashed lines[24] in Fig. 1. This changes the spin-wave density of states at low temperature. Where the density of states is decreased, there is a lower probability for spin-phonon scattering, and the thermal conductivity will improve.

However, if magnons are contributing to the thermal conductivity, decreasing the density of states will lower the conductivity. A magnetic field also changes the temperature at which crossover between the two sets of dispersion curves occurs. The conductivity may first decrease and then increase with field if the crossover point is swept

through the temperature region being studied. Thus, the magnetic field effects will depend on the nature of the dispersion curves, on the magnitude of the field, and on which processes are dominant in the temperature region being studied.

It should be possible to determine the role of magnons in the thermal conductivity from the magnetic field effects described above. However, most crystals will also contain magnetic impurities. These impurities may scatter both phonons and magnons, although probably not at the same rate. If a resonance scattering is involved, a magnetic field could tune the impurity energy levels in and out of resonance. Because these effects would be difficult to separate from intrinsic spin wave behavior, the role of impurities must be carefully considered in the interpretation of magnetic-field-dependent data.

III. EXPERIMENTAL DETAILS

The thermal conductivity measurements were made in ^{3}He, ^{4}He, and adiabatic demagnetization cryostats, and in a dilution refrigerator. Standard techniques were used for the zero-field conductivity.[25] The primary temperature standard in each cryostat was a calibrated germanium resistor. In the ^{4}He cryostat, the sample thermometers were matched pairs of $\frac{1}{10}$-W Allen-Bradley carbon resistors with 110- and 1500-Ω nominal room-temperature resistance. In the other cryostats, 220-Ω $\frac{1}{2}$-W Speer resistors were used.

For measurements in a magnetic field, the carbon resistors were calibrated against capacitance thermometers. These parallel-plate capacitors, fabricated from KCl or NaF doped with OH^- ions, were found to be very sensitive field-independent thermometers.[14] Because their calibration changes with thermal cycling to room temperature, the procedure followed was to take zero-field thermal conductivity measurements, simultaneously calibrating the capacitors and the carbon resistors against the germanium thermometer. A magnetic field was then established and data taken with the carbon resistors now being calibrated against the capacitance thermometers.

It is essential to consider the magnetoresistance of the thermometers when taking data in a field. For the greatest accuracy, they must be calibrated during every run. The technique described here is easier to use and is applicable to lower temperatures than helium-vapor-pressure measurements. Another technique sometimes used is to mount a resistor on a long wire extending to a low-field region of the cryostat. A capacitance thermometer mounted close to the sample was found to be more sensitive to temperature changes at the sample and more stable than such a resistor.

IV. EXPERIMENTAL RESULTS

A. Crystal quality

$RbMnF_3$ crystals were grown in the Cornell Materials Science Center Crystal Growing Facility by the Czochralski technique. The basic procedure has been described in a previous paper.[26]

Thermal conductivity samples about $3 \times 0.3 \times 0.3$ cm^3 and oriented with {100} faces were cut from the single-crystal boules. A typical thermal conductivity curve for samples grown as described in Ref. 26 is shown in Fig. 2 and is labeled singly grown. The Casimir boundary scattering limit for phonons is greater by a factor of 9 at 1 K.

Several variations in the growing procedure were tried in an attempt to improve the crystal quality.[14] Different starting materials were used including zone-refined crystal pieces of RbF and MnF_2. However, only the technique of multiple growing was found to improve the low-temperature thermal conductivity. In multiple growth of the $RbMnF_3$, boules were grown by seed pulling about 75% of the melt, the residual melt and sometimes the ends of the boules were discarded, and two or more boules were remelted together for a second seed pulling. This process could be repeated several times and has been very successful in producing high-quality alkali halides.[18] The thermal conductivity of a typical doubly grown sample is shown in Fig. 2. The conductivity is considerably

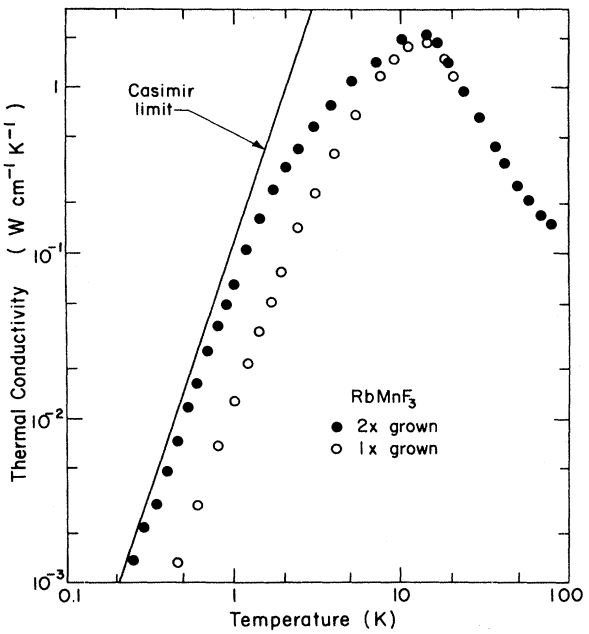

FIG. 2. Thermal conductivity of singly grown and doubly grown $RbMnF_3$. The Casimir limit for phonons is shown for comparison.

better than the singly grown at low temperature, but remains poor around the peak. Seed pulling 4× did not give significantly better thermal conductivity than double growing.

The samples were analyzed for purity and perfection by several methods in addition to thermal conductivity. Several samples were tested and found to be stoichiometric to within the limit of the measurement, which was 1.5%. Etch-pit studies gave dislocation densities of $5 \times 10^5/cm^2$ to $1 \times 10^6/cm^2$, similar to seed-pulled alkali halides.[27] X-ray diffraction indicated the samples were single crystals. The Berg-Barrett x-ray technique was used to search for mosaic structure, which has been blamed for the low thermal conductivity in some magnetic materials including $RbMnF_3$.[11,28] However, no evidence was found for such a structure in these samples.

Table I shows typical impurity levels of either singly or multiply grown boules as determined by spark-source mass spectrometry. The impurity levels are similar to those in multiply grown NaF.[18] Most elements detected have concentrations of less than 10 ppm. This survey shows 10–100 ppm Co. In other samples, Cs, Ni, or Fe might have this concentration. There was no apparent correlation of impurity levels with the growth history of the boule, previous samples grown in the furnace, etc.

Optical-absorption, specific-heat, and low-temperature dielectric-constant measurements were also made to test for impurities. Infrared optical spectra indicated little, if any, OH^- or CN^- went into the crystals even with doping.[29] The specific heat was measured down to 2 K and gave no evidence for a Schottky anomaly. Agreement between the experimental specific heat and the calculated sum of spin plus phonon plus nuclear hyperfine terms indicated that the spin waves were excited and came to equilibrium within the time span of each measurement, which was 1 or 2 min. Only a small concentration, on the order of 1 ppm, of polarizable molecules such as OH^- were detected by dielectric-constant measurements.

From these tests of crystal quality, it appears that the major difficulty in growing pure $RbMnF_3$ is removing elements which substitute pseudoisotopically for either the Rb or the Mn. Figure 3 shows the thermal conductivity of samples doped with K, Fe, Ni, or Co. The magnetic impurities are seen to be particularly effective scatterers: 1800-ppm Fe lowers the conductivity more than does 100 000-ppm K.

TABLE I. Typical spark-source mass spectrometric impurity survey of $RbMnF_3$.

Elements detected	Concentration (ppm atomic)
Co	10–100
Ba, Ca, Ce, Cl, Cr, Cs, Cu, Fe, Gd, Ge, K, Mg, Na, Ni, Ti, V	1–10
As, In, Mo, Rh, Ru, S, Sn, Sr, Y, Zn	0.1–1
Pd, Se, Zr	<0.1

B. Magnetic field dependence, 0.3–2.5 K

The effect of a 5.5-kG magnetic field on the thermal conductivity of $RbMnF_3$ was measured in the temperature range 0.3–2.5 K for singly and doubly grown undoped samples and for samples doped with Fe, Ni, or Co. Figure 4 shows the percent change in thermal conductivity for a 5.5-kG field as a function of temperature. For all of the data shown, the heat flow was in a ⟨100⟩ direction and parallel to the magnetic field. The doubly grown and 1800-ppm Co samples were also measured with the magnetic field perpendicular to the direction of heat flow. In this configuration, the change with field was less than 2% over the entire temperature range.

A solid line is drawn through the data for one of

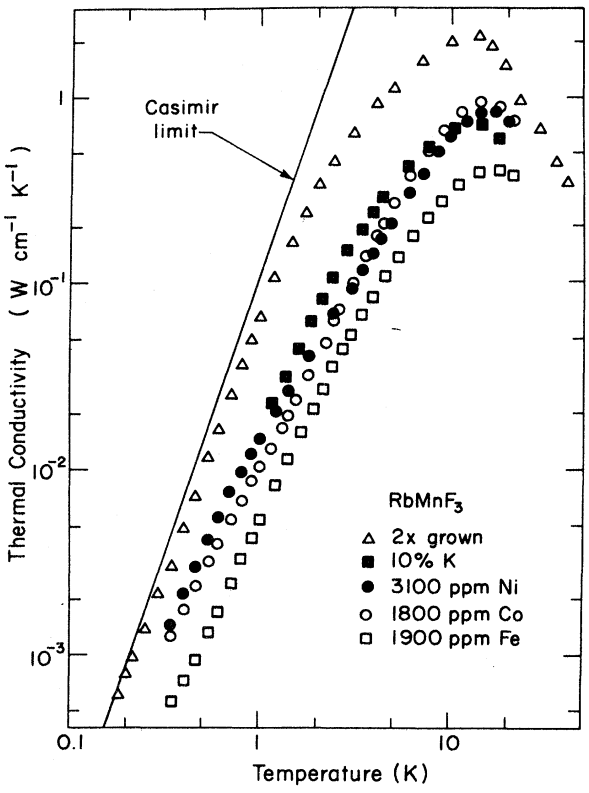

FIG. 3. Thermal conductivity of $RbMnF_3$ doped with K, Ni, Co, and Fe compared with a doubly grown sample.

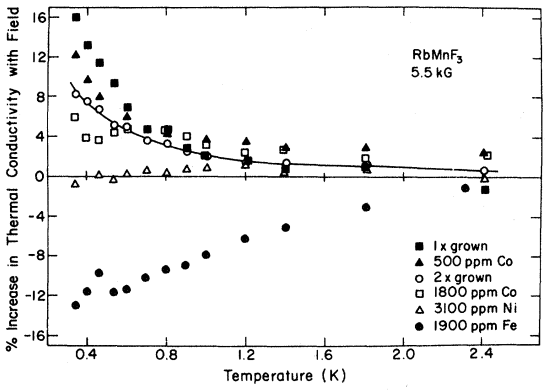

FIG. 4. Percent increase in thermal conductivity with a 5.5-kG magnetic field parallel to the direction of heat flow for several doped and undoped $RbMnF_3$ crystals. Heat flow was in a ⟨100⟩ direction.

the highest-conductivity doubly grown samples. The conductivity increases with the application of a magnetic field, the effect being greater at lower temperature. With doped samples, however, a variety of effects can be observed. The thermal conductivity increases with field in Co-doped samples; with Fe, it decreases; and, with Ni, there is essentially no change. Except for the Ni-doped and the doubly grown samples, the percent change is greater for samples with lower zero-field conductivity.

The changes with field in the doped samples are probably caused by field tunable resonances with the phonons or, possibly, the magnons. With this information, we must conclude that the field effect in the undoped samples may also be caused by some residual impurities rather than being an intrinsic effect. Clearly, the presence of magnetic impurities must be carefully considered in the interpretation of magnetic-field-dependent thermal conductivity.

It should be remarked at this point that these data disagree with previously published work on $RbMnF_3$ by Gustafson and Walker.[30] After some discussion with them about the differences between our results, they sent one of the samples which they used and for which data have been published. Their data could not be duplicated by the technique described here.

It is possible that their results were an impurity effect which had changed with time. We measured the sample over a ten-month period and found no change during this time. Cornell crystals which were measured soon after growth and again up to two years later showed no aging effects. If this was an impurity effect, it is not present in Cornell-grown crystals, and their sample had stabilized by the time we received it.

There are several differences between our methods. Gustafson took measurements as a function of field, taking resistance readings with applied crystal heat while the field was being increased and his isothermal points while the field was decreased. This could be a source of error if his field was not identical for both halves of a given data point. In the Cornell experiments, measurements were taken as a function of temperature at a given field to ensure that the field remained constant throughout the set of data. Also, by taking data this way, we could calibrate the carbon resistors against the capacitance thermometer and directly compute thermal conductivity. Gustafson made corrections for the magnetoresistance in the calculation of each data point, his temperature standard being a resistor mounted on a long wire extending from the sample post to a low-field region of the cryostat. With this arrangement, problems might arise from vibrations, thermal gradients, or eddy-current heating, and, in fact, such problems were observed when we tried this method. The capacitance thermometer which was mounted close to the sample was found to be more stable and more sensitive to small temperature changes at the sample than such a resistor.

The technique employed here was tested by measurement of a nonmagnetic LiF sample: no field effects were observed. Also, data were taken by an alternate method in a ^4He cryostat where the thermometers were calibrated against the vapor pressure. The two sets of data agreed in the temperature region of overlap. Hence, the results presented here are believed to be valid.

C. Measurements for $80 < T < 400$ mK

As discussed in Sec. II, the thermal conductivity of $RbMnF_3$ should be enhanced for $T > 100$ mK by the magnon contribution. In zero magnetic field, crossover between the spin-wave and phonon dispersion curves could depress the conductivity around 180 mK. With an applied field, the conductivity in this region 100–180 mK would be lower than the zero-field value because of the decrease in the magnon density of states as one spin-wave branch is moved to higher energy. However, if magnons were not conducting heat, but were scattering phonons, the conductivity would improve as the density of states decreased in a field.

Measurements were made on two of the highest-conductivity samples down to 80 mK. These measurements were complicated by difficulty in reaching thermal equilibrium. This is explained further in the Appendix. Results for the first sample are shown in Fig. 5. The zero-field thermal conductivity below 180 mK is higher than the Casimir

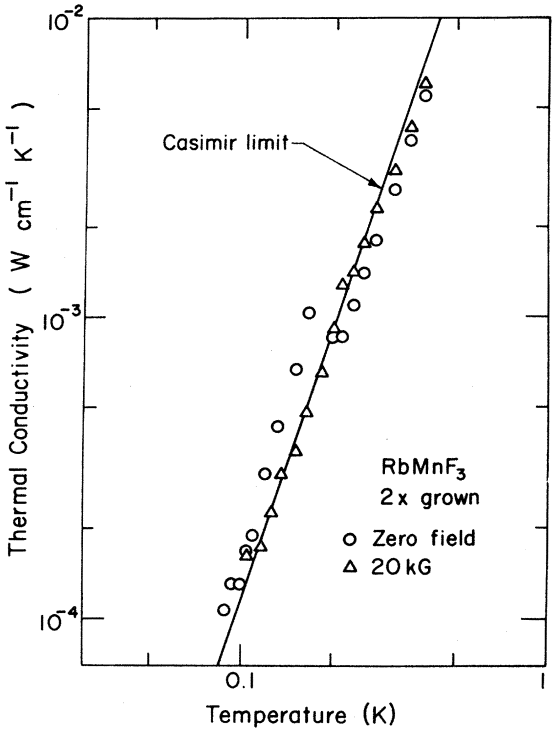

FIG. 5. Thermal conductivity in zero magnetic field and in a 20-kG field for a doubly grown $RbMnF_3$ crystal.

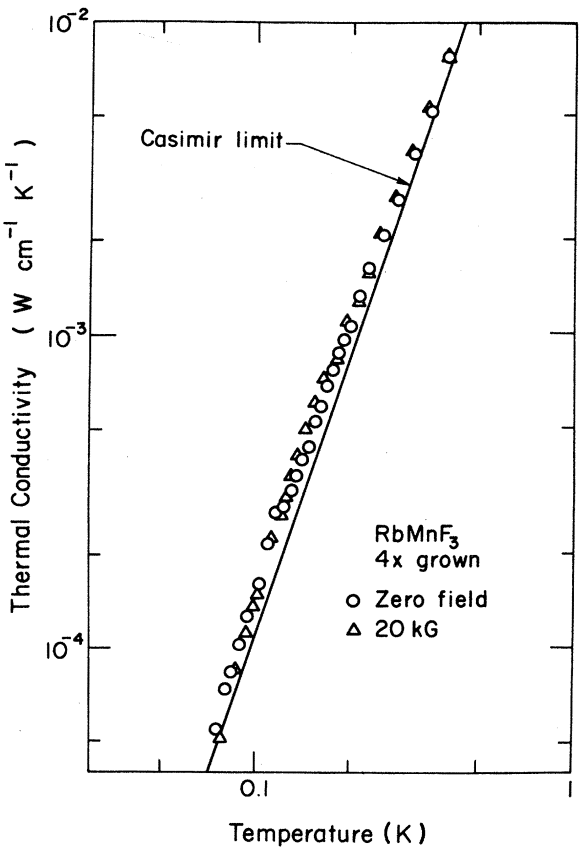

FIG. 6. Thermal conductivity in zero magnetic field and in a 20-kG field for a $RbMnF_3$ crystal which was 4× grown.

limit for phonons alone. With a field of 20 kG the conductivity is depressed in the range 110–180 mK as we expected. A field of 40 kG gave similar results. This sample has higher thermal conductivity than any magnetic crystal previously reported, and its qualitative behavior below 180 mK agrees with that predicted for a magnon contribution.

A second sample, which had been 4× grown, was measured to check these results. Figure 6 shows the data for zero field and 20 kG. The conductivity is about 35% higher than the Casimir value between 100 and 200 mK. The experimental points follow a smooth curve in contrast with the sudden jump at 180 mK for the doubly grown sample. There is no significant change in a magnetic field, which again differs from the results for the first sample.

Both of these samples have thermal conductivity higher than the calculated boundary scattering limit for phonons in a temperature region where there could be a magnon contribution. However, the Casimir limit is an approximation. Corrections for phonon focusing effects have been calculated for several materials.[20] Although the corrections decrease the Casimir value for crystals with anisotropy similar to $RbMnF_3$, for other materials they increase it by as much as 60%. Thus, the high conductivity in the $RbMnF_3$ samples is not necessarily evidence for magnons. Conduction may be entirely by phonons, which are being scattered at the low end of the temperature range studied as well as above 180 mK. In a pure crystal, the magnetic field dependence of the thermal conductivity would confirm the presence of a magnon contribution. However, it appears that some, if not all, of the observed magnetic field effects are caused by impurities since the two samples have quite different behavior in a field.

V. SUMMARY

The experiments on $RbMnF_3$ doped with magnetic impurities have shown that these impurities can depress the thermal conductivity over a wide temperature range and that the conductivity may increase, decrease, or even remain unchanged in a magnetic field, depending on the dopant. These effects are probably caused by field tunable resonances with phonons, or, possibly, magnons.

The field-dependence studies of undoped $RbMnF_3$ for $T<0.3$ K show that two of the best quality sam-

ples can give quite different results. Thus, even crystals with thermal conductivity approximately equal to the Casimir limit for phonons are not pure enough to guarantee that magnetic field effects are caused by magnons rather than by residual impurities. It must be concluded that magnetic impurities are very important factors in the interpretation of thermal conductivity in $RbMnF_3$ and probably also in other magnetic materials.

We have succeeded in growing crystals of better quality than any magnetic materials previously reported. An enhancement of the thermal conductivity above the theoretical boundary scattering limit for phonons was observed for two different $RbMnF_3$ samples in a temperature region where magnons could contribute to the conductivity. This is not necessarily evidence for magnons, however, because the theoretical limit is an approximation.

ACKNOWLEDGMENTS

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APPENDIX

There was no difficulty in reaching thermal equilibrium during the thermal conductivity measurements down to about 160 mK. With decreasing temperature below this point, however, equilibration times became longer, reaching several hours at the lowest temperatures attained. The problem existed for both of the samples measured below 0.3 K and was present in both the adiabatic demagnetization cryostat and the dilution refrigerator. This was attributed to a long nuclear spin-lattice relaxation time. If the spins are only weakly coupled to the lattice, their temperature would not immediately follow changes in the ambient temperature, and a thermal gradient would be set up along the sample as the spin system slowly gave up energy to (or absorbed it from) the lattice.

During one run, the temperature gradient along the sample was monitored as a function of time as the average sample temperature cooled from 101 to 57 mK. From these data and the theoretical lattice thermal conductivity, the approximate heat input to the lattice was calculated. This heat input, 1.3×10^4 ergs, was compared with the nuclear hyperfine energy for a spin-$\frac{5}{2}$ system with the nuclear hyperfine frequency[31] of Mn in $RbMnF_3$. A change in the temperature of the nuclear spins from 200 mK, where they appeared to be in equilibrium with the lattice, to 75 mK would supply this energy.

The time constant associated with the heat input to the lattice increased from 0.33 h at a lattice temperature of 100 mK to 3.7 h at 57 mK. The theoretical nuclear spin-lattice relaxation rate T_1^{-1} has been studied for relaxation via hyperfine interactions between the nuclear spins and the electronic spin-wave spectrum in ferro- and antiferromagnets.[32-34] The direct process in which a single magnon is emitted or absorbed is not allowed on the basis of energy conservation. Theoretical curves of T_1^{-1} as a function of temperature for Raman and higher-order processes exhibit a sharp drop in T_1^{-1} below the temperature T_{AE} of the anisotropy-exchange gap in the magnon spectrum. Experimental values of T_1^{-1} for ^{19}F in MnF_2, which has $T_{AE}=12.5$ K, were compared with theory by Kaplan *et al.*, and excellent agreement with the theory for the direct Raman process was found.[35] At 3.1 K $=0.25T_{AE}$, the relaxation time was 0.28 h. This is comparable to our value of 0.33 h at $T=0.27T_{AE}$ in $RbMnF_3$.

If the hyperfine interaction is isotropic, as in $RbMnF_3$, only higher-order processes than direct Raman would be allowed. This situation applies to ^{57}Fe in the ferrimagnet YIG and ^{19}Mn in the hexagonal antiferromagnet $CsMnF_3$. Relaxation rates have been measured in these materials by resonance techniques and compared with theory.[36,37] In YIG, T_1 at 2 K was observed to be 0.43 h. In $CsMnF_3$, T_1 at 1.4 K with an applied magnetic field of 0.5 T was 3.7 sec and was following a temperature dependence of $T^{-4.96}$. For this field, $T_{AE}=0.69$ K. Agreement with theory was unsatisfactory for these two materials, indicating some other relaxation processes may be important.

There is evidence that the existence of a nuclear spin-wave spectrum may be important in nuclear relaxation.[38-40] This has been examined in particular for $RbMnF_3$, but only for specific experimental situations inapplicable to the present experiment.[38] Further theoretical studies of this process, including examination of the temperature dependence of the relaxation rate, would be of interest. Meanwhile, comparison of the $RbMnF_3$ results with those described above for other materials, indicates that the long temperature-dependent relaxation times observed are not unreasonable for a nuclear spin system in a magnetic material.

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*Present address: Dept. of Phys. Oklahoma State University, Stillwater, Okla. 74074.

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