Measurements of the Specific Heats of Three Magnetic Salts at Low Temperatures*

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New experimental results are presented of the heat capacity of chromium potassium alum, ferric ammonium alum, and manganese ammonium Tutton salt below 0.7°K. They have been obtained using two different experimental methods which differ in the way in which the samples are placed in thermal contact with the cerium magnesium nitrate thermometer and the electrical heater. λ -type transitions were found at 0.0260°K in FeNH4 alum and at 0.173°K in Mn(NH4)2 Tutton salt. The heat capacity of CrK alum, measured to 0.017°K, is a good fit to the theory of O'Brien using paramagnetic resonance parameters suggested by Bleaney. The entropy of each salt has been calculated from the specific-heat data, and a comparison with previous work is presented. An estimate of the thermal resistance between the paramagnetic crystals and He4 is obtained.

I. INTRODUCTION

FOR many years the properties of paramagnetic salts have been the subject of extensive work. Among the most studied substances are potassium chromium alum [CrK(SO₄)₂·12H₂O], ferric ammonium alum [FeNH4(SO4)2·12H2O], and manganese ammonium Tutton salt [Mn(NH₄)₂(SO₄)₂·6H₂O]. Comprehensive reviews of the properties of these and other substances have been published by de Klerk¹ and Ambler and Hudson,² among others.^{3,4}

Although this previous work has contributed substantially to the understanding of many phenomena which occur in these salts, there is very little quantitative agreement between different authors, particularly in regard to the dependence of the entropy and specific heat on the absolute temperature.

It is the purpose of this paper to present measurements made using a simple technique⁵ of the specific heat of the above three salts and to compare these measurements and the calculated entropies both with the measurements of other authors and with existing theories.

II. EXPERIMENTAL METHOD

Two different experimental techniques were used for obtaining thermal equilibrium between sample, heater, and thermometer. One uses liquid He⁴ as thermal contact agent and has been described by Vilches and Wheatley.⁵ The other uses a greased contact with copper wires and has been described by Anderson, Salinger, and Wheatley.⁶ Only a summary of these techniques will be given here. The absolute temperature is measured by means of a cerium magnesium nitrate (CMN) thermometer. Known quantities of heat are applied with an electrical heater. In the experimental arrangement using He⁴ as contact agent, the CMN thermometer was in the form of a powder of typical grain size 0.1 mm, and the sample was in the form of little crystals, mostly smaller than 1 mm³. These were placed inside an Epibond 100A7 cell whose inner wall was lined with 1050, 0.05-mm-diam Formex insulated copper wires (Fig. 1). Sample and thermometer were separated in space so the magnetism of the sample would not interfere with the temperature measurements. The heater, made of 0.05-mm-diam Evanohm⁸ wire, was wound around a cotton cloth cylinder and glued to it with a mixture of GE 7031 varnish and toluene. A resistance thermometer⁹ was used as a temperature indicator during magnetizations. The copper wires embedded in the inner wall of the cell were hard soldered to three 1-mm-diam copper wires, which in turn were soft soldered together. A lead¹⁰ or tin strip was soldered to these wires and to a He³ refrigerator and provided the thermal contact for magnetizations. The cell was filled with liquid He⁴ via a $\frac{1}{64}$ -in. o.d. $\times 0.003$ -in. wall 70-30 cupronickel tube that was connected thermally both to the He³ refrigerator operating at 0.3°K and to a 20-g FeNH₄ alum thermal guard placed between the He³ refrigerator and the cell. Details are given by Vilches and Wheatley.⁵

The experimental arrangement (Fig. 2) using a greased contact was designed for measurements above 0.1°K. The salts in the form of slabs between 2.5 and 3 mm thick were glued with Apiezon "N" grease¹¹ on

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¹D. de Klerk, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. XV, p. 38. ²E. Ambler and R. P. Hudson, Rept. Prog. Phys. 18, 251

 ⁴W. A. Little, Progress in Cryogenics (Academic Press Inc., New York, 1964), Vol. 4, p. 99.
 ⁴A. H. Cooke, Progress in Low Temperature Physics, edited by A. H. Cooke, Progress in Low Temperature Physics, edited by

C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1955), Vol. I, p. 224.

⁵O. E. Vilches and J. C. Wheatley Rev. Sci. Instr. 37, 819 (1966).

⁶ A. C. Anderson, G. L. Salinger, and J. C. Wheatley, Rev. Sci. Instr. 32, 1110 (1961).
⁷ Epibond 100A is an epoxy resin distributed by Furane Plastics, Inc., 4516 Brazil Street, Los Angeles, California.
⁸ Wilbur B. Driver Co., Newark, New Jersey.
⁹ Nominal 100 Ω, ¹/₄ W, grade 1002, Speer Carbon Company.
¹⁰ W. Reese and W. A. Steyert, Rev. Sci. Instr. 33, 43 (1962).
¹¹ James G. Biddle Company, Township Lane and Jolly Road, Plymouth Meeting Pennsylvania

Plymouth Meeting, Pennsylvania.



FIG. 1. Cell used for the specific-heat measurements with small crystals and liquid He4. A, FeNH4 alum thermal guard. B, Lead switch. C, Copper wires inner wall. D, Speer resistor. E, Heater. F, Cotton cloth. G, He⁴ filling tube.

one end of coil-foil strips.¹² The other end of the coil-foil strip was separated like a brush, dissolving the GE 7031 varnish, and the wires were mixed with a mixture 2:1 by weight of powder CMN and Dow-Corning 200 silicone oil, 20 000 cp viscosity.¹³ The temperature measurements were made with a 17-cps mutual inductance bridge. The technique has been described in detail.¹⁴ The magnetic thermometer was calibrated in the He⁴ temperature range.

The specific heat points were taken applying heat during known time intervals and measuring the temperature jumps with the CMN thermometer. The heat supplied per second was measured with a Leeds and Northrup type K-3 potentiometer.¹⁵ The time during which the power was on was measured with an Anadex counter-timer model CF-200R¹⁶ connected to the heater switch.

The CrK alum samples for the cell were prepared rolling the small crystals as they came in a jar¹⁷ over moistened filter paper, until they had a dark color (see Ref. 5 for a full description). The FeNH₄ alum¹⁷ and Mn(NH₄)₂ Tutton salt¹⁸ cell samples were small single crystals grown from saturated solutions.

For the ferric alum all the crystals were smaller than 2.2-mm maximum "length" and for the Tutton salt all were smaller than 1 mm. The average size of the CrK alum crystals was around 0.5 mm. A more precise estimate of the size of the crystal was made later in order to estimate the sample surface in contact with the He⁴ in the cell.



FIG. 2. Experimental arrangement for measurements above 0.1°K. A, Tef-lon support. B, Copper wire for soldering a lead switch. C, Slabs of crystals. D, Coil-foils. E, Nylon spatula. F, Speer resistor. G, Evanohm heater. H, Copper wires from the coilfoils. I, Mixture of powdered CMN and Dow-Corning 200 Fluid, 20 000 cs.

¹⁵ Leeds and Northrup Co., Philadelphia, Pennsylvania.

 ¹⁶ Anadex Instruments, Inc., Van Nuys, California.
 ¹⁷ Baker Analyzed Reagent, J. T. Baker Chemical Co., Phillipsburg, New Jersey

Made with Mn sulfate, A.C.S. Code 1957, Allied Chemical, Morristown, New Jersey, and (NHJ)2 sulfate, Analytical Reagent, Mallinckrodt Chemical Works, New York, New York.

¹² Coil-foil is a sheet made with thin copper wires glued together with a mixture of the adhesive GE 7031 and toluene. ¹³ Dow-Corning Corporation, Midland, Michigan.

¹⁴ W. R. Abel, A. C. Anderson, and J. C. Wheatley, Rev. Sci. Instr. 35, 444 (1964).

III. RESULTS

Two samples of CrK alum, one of FeNH₄ alum, and one of $Mn(NH_4)_2$ Tutton salt were investigated with the cell method. Their weight was 9.69 g, 10.87 g, 5.00 g, and 9.43 g, respectively. One sample of each salt was measured with the slabs technique, their weights being 6.90 g for the CrK alum, 6.52 g for the FeNH₄ alum, and 6.69 g for the Tutton salt. In the case of the He⁴ cell method using CrK alum, immediately after the demagnetization (from about 0.35°K and 10 000 G) the CMN thermometer cooled down below $T^* \approx 0.003$ °K, the limit of our measuring coils. Over 60 000 sec passed before the CMN came into equilibrium with the sample at about 0.013°K. This lack of thermal contact between the sample and the thermometer was later turned to our advantage in measurements of the superconductivity of tungsten.¹⁹ Heat capacity measurements were attempted from $T \approx 0.013$ °K, but the thermal time constants for equilibrium within the cell were too long to yield reliable results. Very reproducible points started at 0.017°K, and from there on they are represented in Fig. 3. At this temperature, after turning off the heater, the time for equilibrium to be established in the cell was about 1300 sec. This time diminished continuously as the temperature rose. At 0.05°K it was negligible. Data were taken continuously for over 24 h, until the negative heat leak from the colder surroundings into the sample was too large. This limit was around 0.4°K. At this temperature the heat capacity of the He⁴ filling the cell was also a substantial amount of the measured heat capacity. Several demagnetizations were made from different temperatures and fields, in order to start measuring at different temperatures. Always we found the same experimental values for the specific heat after each demagnetization independent of the history of the sample. With the slabs technique heat was supplied until the temperature was slightly above 0.1 °K. From there on points were measured continuously also until the failure of the thermal isolation of the sample. This limit was around 0.7 °K. No discrepancies were found in the values measured in the three samples with the two methods. The slabs' results are also indicated in Fig. 3.

With the cell and FeNH₄ alum, the minimum temperature was slightly below 22 m°K. A λ -type anomaly was measured with $T_{\lambda} \approx 0.026$ °K (see Fig. 3). Very near the λ point, but below it, the thermal equilibrium times increased continuously, being of the order of 6000 sec just below the transition. Above the transition, the equilibrium times decreased rapidly to values comparable with the ones for CrK alum. This phenomenon made measurements near the λ point very difficult and contributed to the scatter of the measured points. Measurements were made both with the He⁴ cell and



FIG. 3. The specific heats of CrK alum, FeNH₄ alum and Mn- $(NH_4)_2$ Tutton salt as a function of the absolute temperature.

with the slabs in the same way as for CrK alum, and both types show excellent agreement.

With Mn(NH₄)₂ Tutton salt, a minimum temperature of 0.09°K was reached after demagnetization. A λ -type anomaly was measured with the He⁴ cell and with the slabs with $T_{\lambda} \approx 0.173 \,^{\circ}\text{K}$ (Fig. 3). No increase in the time constants near the transition was found with the He⁴ cell and the small crystals, the time for equilibrium being negligible. However, very large time constants were found with the slabs, the last measured point below the transition having an equilibrium time of 13 000 sec. Above the transition, the slabs' equilibrium times became comparable with those for the alums. The lack of agreement between the results from slabs and small crystals below the transition is probably due to the long time constants. Above the transition the agreement between both sets of results is excellent.

The heat leak to the He⁴ cell was small. At 17 m°K it was about 3 erg/min, and it was smaller at higher temperatures. The heat leak during the experiments with slabs was of the order of 6 erg/min at 0.1°K.

A background heat-capacity measurement was made using a tin superconducting switch between the iron alum thermal guard and the cell. In this way the cell was cooled to about 0.05°K by the thermal guard. Immediately after demagnetization, the cell warmed very rapidly. The few points measured indicated a very

¹⁹ R. T. Johnson, O. E. Vilches, J. C. Wheatley, and S. Gygax, Phys. Rev. Letters **16**, 101 (1966).



FIG. 4. The measured specific heat of CrK alum as a function of the absolute temperature, compared to calculated curves using paramagnetic resonance data. O Cell, first sample. Δ Cell, second sample. + Slabs. ----- Calculated usin g Bleaney's paramagnetic resonance data and assumed percentages of ions with different splittings (30% of the ions with $\delta_1=0.388^\circ$ K, 30% with $\delta_3=0.22^\circ$ K, and 40% with δ_3 = 0.05°K). --- Calculated curve assuming 28% of the ions with $\delta_1, 28\%$ with δ_2 , and 44% with δ_3 .

FIG. 5. The entropy of CrK alum as a function of the absolute temperature. Calculated from our heat capacity data. \bigcirc Measured by Bleaney. -- Measured by Daniels and Kurti. -- Measured by Beun, Miedema, and Steenland.

small heat capacity that could be accounted for within 20% by the sum of the calculated heat capacities of the CMN thermometer,²⁰ of the He⁴ in the cell,²¹ and of the epoxy Epibond 100A.²² It was assumed that one could

²⁰ J. M. Daniels and F. N. H. Robinson, Phil. Mag. 44, 630 (1953).

²¹ H. A. Kramers, J. D. Wasscker, and C. J. Gorter, Physica 18, 329 (1952).

 22 No results have been reported on the specific heat of Epibond 100A. We used the value measured for Araldite (a material similar to Epibond 100A) by D. M. Parkinson and J. E. Quarrington, Brit. J. Appl. Phys. 5, 219 (1954).

calculate the calorimeter background corrections for the high temperature points. The points in Fig. 3 have already been corrected. The slab points were corrected for the heat capacities of the nylon support²³ and the copper²⁴ in the coil-foils. All other calculated corrections were negligible.

²³ Specific heat of nylon: 2567³ erg/cm³ °K, W. Reese (private communication). ²⁴ Wright Air Development Division Technical Report 60-56,

²⁴ Wright Air Development Division Technical Report 60-56, Edited by V. J. Johnson (Armed Services Technical Information Agency, Arlington Hall Station, Arlington 12, Virginia), Part II, p. 4.112-1 (unpublished).





IV. DISCUSSION

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The agreement between the heat capacity results for the different samples of CrK alum is excellent. In view of past observations that different samples of this alum yield different results,¹ the agreement between different samples is particularly remarkable considering the completely different way in which the He⁴ cell samples and slabs were prepared. There is not a broad maximum in CrK alum's heat capacity around 0.1°K as measured by Bleaney²⁵ or a sharp one at 0.135°K as calculated by Beun, Miedema, and Steenland²⁶ from their measured S-versus-T curve. Furthermore, general agreement down to 0.2°K with the Hebb and Purcell²⁷ theory based on a single splitting $\delta = 0.24$ °K. of the lowest quadruplet does not exist in the present work. Instead a substantial agreement is found with the calculated specific heat, using the two splittings that Bleaney²⁸ measured using paramagnetic resonance and the third that he assumed in order to match the $1/T^2$ coefficient of the specific heat above 1°K, using 30% of the ions with $\delta_1 = 0.338$ °K, 30% with $\delta_2 = 0.22$ °K, and 40% with $\delta_3 = 0.05$ °K. If one assumes that the dipole-dipole contribution to the specific heat can also be divided in the same way using O'Brien's²⁹ and Hebb and Purcell's²⁷ results, one can calculate a specific heat that is illustrated in Fig. 4. This calculated curve has the same shape as the measured curve, and is not very different from it down to 0.03°K. Assuming that 28% of the ions have δ_1 , 28% have δ_2 , and 44% have δ_3 , a slight variation of the percentages of ions with different splittings, the calculated curve and the measured curve will superpose down to 0.07°K, and be even closer than with Bleaney's proposed percentages down to 0.03°K. The entropy, calculated from the heat capacity curve, is displayed in Fig. 5 and compared with the ones measured by Bleaney,25 Daniels and Kurti,30 and Beun, Miedema, and Steenland.26 The value of CT^2/R is not constant even at the highest measured temperature. At 0.69°K it is increasing very slowly, its value being 0.0159°K². This is in fair agreement with the value of 0.0162°K² measured by Kapadnis.³¹

The heat capacity of FeNH₄ alum increases with decreasing temperature up to a more or less constant value around 0.06°K. There is no pronounced minimum immediately above the λ point as estimated by Kurti

 ²⁵ B. Bleaney, Proc. Roy. Soc. (London) A204, 216 (1950).
 ²⁶ J. A. Beun, A. R. Miedema, and M. J. Steenland, Physica 23, 1 (1957).
 ²⁷ M. H. Hebb and E. M. Purcell, J. Chem. Phys. 5, 338 (1937).
 ²⁸ D. Bleaner, Phys. Rev. C 4021 (2017) (1977).

²⁸ B. Bleaney, Proc. Roy. Soc. (London) A204, 203 (1950).

²⁹ M. C. M. O'Brien, Phys. Rev. 104, 1573 (1956).

³⁰ J. M. Daniels and N. Kurti, Proc. Roy. Soc. (London) A221, 243 (1954)

³¹ D. G. Kapadnis, Physica 22, 159 (1956).



FIG. 7. The specific heat of $Mn(NH_{4})_2$ Tutton salt very near the transition, as a function of $\log |T-T_{\lambda}|$. \bigcirc Below the transition. \square Above the transition.

and Simon.³² Because of the long time constants, it was not possible to study the nature of the transition with any precision. The entropy was calculated from the



FIG. 8. The entropy of $Mn(NH_4)_2$ Tutton salt as a function of the absolute temperature. — Calculated from our heat-capacity data. × Measured by Cooke and Hull (reported by Cooke). \bigcirc Measured by Miedema, van den Broek, Postma, and Huiskamp.

³² A. H. Cooke, Proc. Phys. Soc. (London) A62, 269 (1949).

heat capacity curve. It is shown in Fig. 6 with the entropies measured by Kurti and Simon³² and by Steenland, de Klerk, Potters, and Gorter.33 For calculating across the λ point, a logarithmic type of singularity was assumed. Although the absolute temperature at which the transition occurs, as given by the different authors, is not the same (this work: 0.026°K, Kurti and Simon: 0.043°K, and Steenland et al.: 0.030°K) the entropy at the transition is about the same (S/R=0.69,0.65, and 0.64, respectively). If one uses Kurti and Simon's S-versus- T^* curve and Cooke, Meyer, and Wolf's³⁴ T-versus- T^* values for this salt, the resulting S-versus-T curve is in good agreement with the one we calculated above T = 0.045 °K. There is no complete theory with which our results can be compared. Hebb and Purcell,27 under the assumption of a cubic field that will split the ground level into a doublet and a quadruplet, found moderate agreement with early experimental results.³⁵ Later paramagnetic resonance³⁶ and paramagnetic relaxation³⁷ experiments could only be explained under the assumption of a trigonal field³⁸ in addition to the cubic field, the effect of this field being to split the ground level in three doublets. No detailed theory for the effect of the dipolar interaction on the

³³ M. J. Steenland, D. de Klerk, M. L. Potters, and C. J. Gorter, Physica 17, 149 (1951).

³⁴ A. H. Cooke, H. Meyer, and W. P. Wolf, Proc. Roy. Soc. (London) **A233**, 536 (1956). ³⁵ N. Karti and R. S. Barr, Proc. Roy. (London) **A140**.

³⁵ N. Kurti and F. Simon, Proc. Roy. Soc. (London) **A149**, 152 (1935); **A152**, 21 (1935).

³⁶ J. Ubbink, J. A. Poulis, and C. J. Gorter, Physica 17, 213 (1951).
³⁷ R. J. Benzie and A. H. Cooke, Proc. Phys. Soc. (London)

⁴⁶³, 213 (1950).

heat capacity analogous to that of O'Brien has been worked out for this salt. Our data seem to correspond with the possibility of the three doublets nearly equally spaced, if the interactions are not too strong. The measured value of CT^2/R is always increasing with temperature up to 0.7°K, the last value being 0.0125°K². The value measured by Kapadnis³¹ was 0.0135°K².

The dominant characteristic of the heat capacity of $Mn(NH_4)_2$ Tutton salt is the λ -type anomaly in the specific heat at 0.173°K. Points were taken to about $10^{-3}~^{\circ}\mathrm{K}$ from the transition. Between 10^{-2} and $10^{-3}~^{\circ}\mathrm{K}$ from the transition, a plot of the specific heat versus $\log |T - T_{\lambda}|$ gives two straight lines for the points above and below the transition, both having different coefficients (Fig. 7). Using the He⁴ cell method more precise measurements closer to the transition could be made possible just by increasing the size of the thermometer. The electronic entropy was calculated from the measured specific-heat curve, assuming a logarithmic singularity at the transition. The result, compared with those obtained by Cooke and Hull³² and Miedema, van den Broek, Postma, and Huiskamp,39 is shown in Fig. 8. As in the case of the iron alum, a substantial disagreement is found between the different measurements in the temperature of the transition, but good agreement is found as to the entropy at which this transition occurs in all of the cases (Cooke and Hull³²: S/R=1.27 and T=0.15°K; Steenland et al.⁴⁰: S/R= 1.28 and $T = 0.12^{\circ}$ K; Miedema *et al.*³⁹: S/R = 1.25 and T=0.14°K; and this experiment: S/R=1.27 and T=0.173 °K). The value of CT^2/R is almost constant between 0.27°K and the highest measured temperature,





⁴⁰ M. J. Steenland, L. C. van der Marel, D. de Klerk, and C. J. Gorter, Physica 15, 906 (1949).



its value being 0.030 °K². The value obtained by Cooke and Hull²² was 0.033 °K².

An estimate of the Kapitza thermal resistance between He⁴ and the crystals of CrK alum and FeNH₄ alum can be made using the original data (Fig. 9). When the heater is on, the He⁴ and the CMN thermometer warm to a temperature above that of the sample. After the initial transient one can assume approximately that the CMN measures the increased temperature of the He⁴ needed to drive the heat into the sample. When the heater is turned off, the CMN and He⁴ cool to the sample temperature again. Taking the difference in temperature between the point at which the heater was turned off and the extrapolation of the final equilibrium curve as ΔT , and the measured rate at which heat was being transferred as \dot{Q} , an effective thermal resistance $\Delta T/\dot{Q}$ can be calculated. Figure 10 shows a plot of $\ln \Delta T/\dot{Q}$ as a function of $\ln T$. The surface area of the samples was estimated after evaluating the size distribution of the small crystals. One finds for CrK alum

$$\left(\frac{\Delta T}{\dot{Q}}\right) \approx \frac{5 \times 10^{-6}}{A T^3} \frac{^{\circ} K^4 \text{ cm}^2}{\text{erg/sec}}, \quad 0.017^{\circ} \text{K} < T < 0.035^{\circ} \text{K}; \quad (1)$$

and for FeNH₄ alum

$$\frac{\Delta T}{Q} \approx \frac{1 \times 10^{-5}}{A T^{2.8}} \frac{K^{3.8} \text{ cm}^2}{\text{erg/sec}}, \quad 0.023^{\circ} \text{K} < T < 0.044^{\circ} \text{K}. \quad (2)$$

If one fits a $1/T^3$ law to the highest points of FeNH₄ alum (Fig. 10), then

$$\frac{\Delta T}{\dot{Q}} \approx \frac{5 \times 10^{-6}}{A T^3} \frac{^{\circ} K^4 \text{ cm}^2}{\text{erg/sec}}, \quad 0.023^{\circ} \text{K} < 0.044^{\circ} \text{K}. \quad (3)$$



FIG. 11. The increase of the effective thermal resistance between crystals and He⁴ near the λ transition in FeNH₄ alum.

It is probable that the above equations for $\Delta T/\dot{Q}$ represent an actual boundary resistance between the liquid He⁴ and the magnetic salt crystals. This remark is based on the results of a more detailed analysis by Anderson, Salinger, and Wheately⁶ of the problem of heat transfer via a greased contact into slabs of chromium potassium alum. These authors deduced that the

temperature discontinuity occurred at the surface of the crystals. For this to be so, the coupling between spins and phonons must be sufficiently weak that a single phonon temperature is valid for the whole crystal. In such a case a thermal diffusion process, characterized by a thermal relaxation time

$$\tau = l^2 C / \kappa \,, \tag{4}$$

where l is a characteristic crystal size, C is the heat capacity per unit volume, and κ is the thermal conductivity, does not occur. Rather heat is transferred from a "bath" external to the crystal via the boundary resistance to a phonon "bath" in the crystal and then via the spin-lattice resistance to the spin "bath". Near a λ point, however, this picture may break down as a result of an enhanced spin-phonon interaction. Evidence for this in the case of ferric alum in the immediate vicinity of 0.026°K is shown in Figs. 10 and 11. Here the effective resistance is seen to increase sharply over the extrapolated boundary resistance. This increase may be interpreted as evidence for the development of a thermal-diffusion-limited heat transfer within the crystal and a resulting "hot" shell at the surface of the crystal which requires more temperature difference to drive the same heat flux into the crystal. Evidence for an enhanced phonon scattering near a magnetic cooperative transition has been seen before, for example, by van Kempen, Miedema, and Huiskamp⁴¹ in K₃Fe-(CN)₆ near its magnetic anomaly at 0.13°K. The thermal diffusion process also explains the difficulty of making measurements using large single crystals of manganese Tutton salt and greased contacts near the λ point of this salt. Since the thermal relaxation time, Eq. (4), is proportional to the square of the crystal size, one expects the relaxation time to be almost two orders of magnitude larger for the large crystals used in the greased contact compared with the small ones used in the He⁴-cell method.

 $^{^{41}\,\}mathrm{H.}$ van Kempen, thesis, University of Leiden, 1965 (unpublished).