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Magnetization, Velocity of Sound, and Specific Heat of Sc_3In

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The magnetization at 1.5 and 4.2 °K and the velocity of sound in zero field of Sc_3In from 1.5 to 300 °K and in applied fields at 1.5 and 4.2 °K are reported. The magnetic behavior exhibits essentially no coercive field, remanence, or hysteresis. A thermodynamic formula is obtained relating the field dependence of the velocity of sound with magnetostriction and magnetic susceptibility. A qualitatively successful comparison is made using our results and the magnetostriction data of Fawcett and Meincke. Specific-heat data at zero field and 1.3 kOe are reported and are related thermodynamically to the magnetization data.

I. INTRODUCTION

Sc_3In (nominal composition) exhibits magnetic behavior at low temperatures which is critically dependent upon composition.[1] Magnetization in fields greater than 1 kOe and pressure measurements have recently been reported.[2] The magnetization, field dependence of the velocity of sound in the magnetic state, and the specific heat are reported here. We find the magnetic behavior shows (i) approximately zero coercive field and zero remanence, (ii) an initial susceptibility $d4\pi M/dB \sim 1$ (corresponding to ferromagnetism), and (iii) no hysteresis. The latter behavior allows a qualitatively successful thermodynamic comparison of velocity-of-sound results with the static magnetostrictive data of Fawcett and Meincke.[3] It is also concluded that if magnetic domains exist in this sample their size is less than $\sim 10\ \mu$. The specific heat shows (i) neither a latent heat nor a strong second-order-transition singularity at the Curie point, (ii) a magnetic field dependence which is in reasonable agreement with thermodynamic predictions from magnetization data, and (iii) a behavior above the Curie point which is in disagreement with the predictions from the elastic data.

Samples were prepared by melting in an arc furnace followed by an annealing in an evacuated quartz tube for about 1 week at 850 °C. The magnetic behavior compared well with previously reported data.[2]

II. MAGNETIZATION

Static-field magnetization data[4] between 100 Oe and 14.5 kOe at 4.2 °K for our polycrystalline sample are shown in Fig. 1. These results as well as the 1.5 °K data agree with those reported earlier by Gardner *et al.*[2] To complete the magnetization data to zero field, calibrated ac susceptibility measurements were made at 200 Hz and 1 kHz. The low-field data at $T = 1.8$ °K are shown in Fig. 2. These measurements showed (i) a zero-field susceptibility $d4\pi M/dB \approx 1$ corresponding to ferromagnetism,[5] (ii) a coercive field of less than 1 Oe, and (iii) no frequency dependence or hysteretic effects. Integrating the ac susceptibility results (on the basis of no hysteresis) showed (i) a remanence of zero (to within 5 G) and (ii) a moment at 100 Oe in agreement with that obtained by static measurements to within the estimated error of 10%. These results, in summary, show that the moment extrapolates to zero with zero-field slope $d4\pi M/dB \approx 1$ (see Fig. 1)[6] or, equivalently, $dM/dH_a \approx 1/D$, where H_a is the applied field and D is the demagnetizing factor.

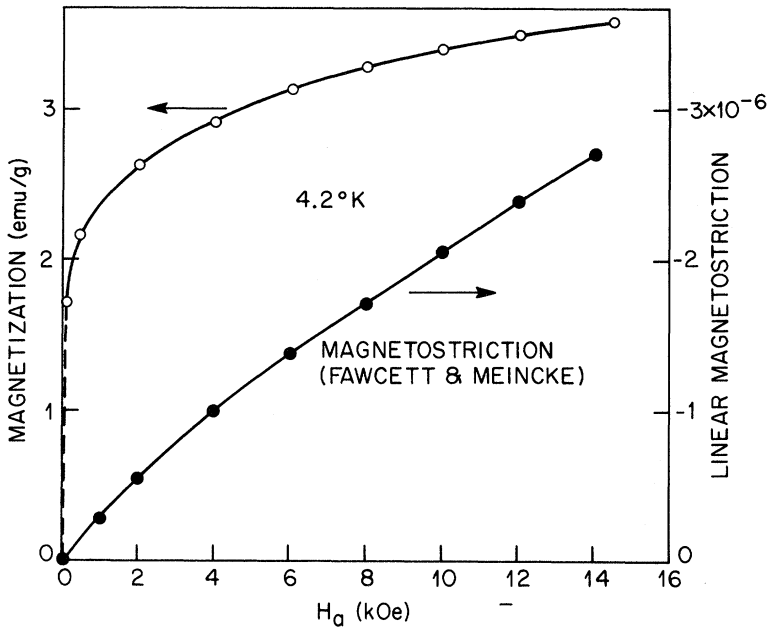

FIG. 1. Magnetostriction (data of Fawcett and Meincke, Ref. 3) and magnetization vs applied field for Sc_3In. The solid and dashed lines for the magnetization data refer to static and ac measurements, respectively.

III. VELOCITY OF SOUND

The temperature dependence of the velocity of longitudinal and transverse sound at 20 MHz in our polycrystalline sample is shown in Fig. 3. Magnetic ordering is expected in this material at T between ~5.6 and 7.5 °K (see Sec. IV). A slight softening in the velocity-of-sound data occurs below 20 °K for longitudinal waves, and below 9 °K for transverse waves. The magnitude of this precursor effect is relatively small compared to other magnetic transitions. Below 4.2 °K a small negative (and normal) temperature coefficient of the velocity of sound occurs.

The fractional increase in the velocity of sound V_L ($\approx 5.08\times10^5$ cm/sec) with magnetic field at 4.2 and 1.5 °K for the same sample is shown in Fig. 4. These data are for longitudinal waves at 20 MHz and, to within the indicated noise, are independent of the angle between the propagation and applied field directions. The error in the sound velocity is ~5% and that of the field data was ~10%. These large errors were due to a poor echo pattern in the pulse-echo technique used—a probable result of some sample inhomogeneity.

The results in Fig. 4 (see insert) show that for

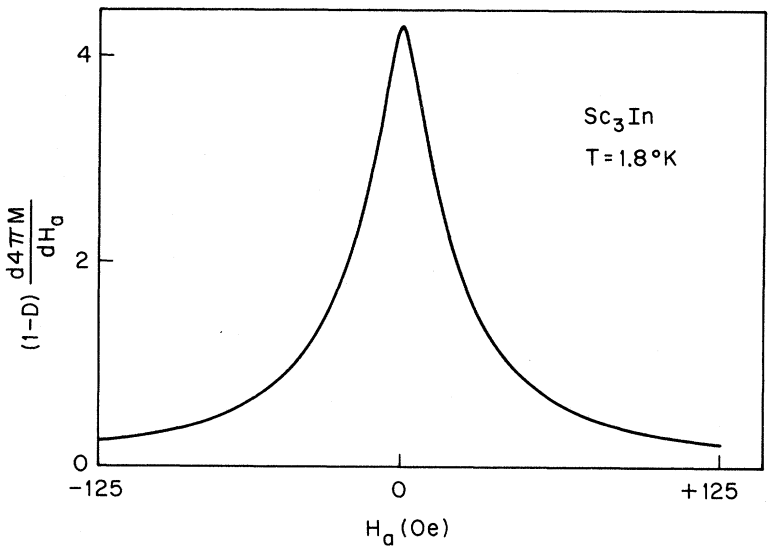

FIG. 2. Differential susceptibility $(4\pi - D)\, dM/dH_a$ vs applied field at $T = 1.5$ °K. The demagnetizing factor is $D \sim 1.9$ for this sample. The reverse field trace superposed the forward trace to within the time constant of the circuitry (equivalent to less than 1 Oe in this case).

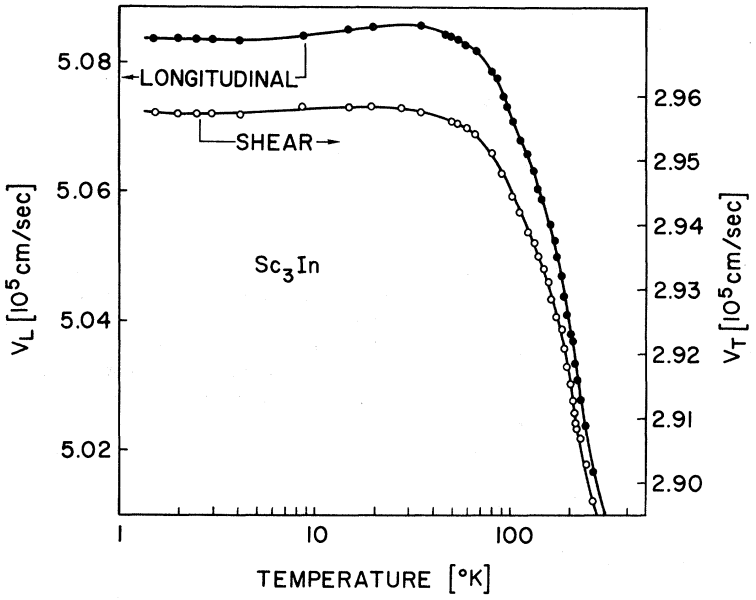

FIG. 3. Temperature dependence of the longitudinal and shear (transverse) velocity of sound in polycrystalline Sc_3In.

the smallest applied fields of either sign for which the measurements were reliable (~ several oersted) a linear increase in V_L occurs. To within this uncertainty in field no hysteresis (i.e., coercive field) with reverse field sweep, and no dependence on field-sweep rate (from 10 Oe/sec to 1 kOe/sec) were found. This is, again, contrary to the usual hysteretic effects in magnetic materials which are readily observable even in high-frequency velocity-of-sound experiments. Normally, the effects which arise from hindered domain-wall motion become so large at high frequencies that ultrasonic behavior is dictated by domain-wall dynamics and cannot be related to the static properties by thermodynamic arguments. The lack of observed hysteresis in Sc_3In suggests, however, that such relations may apply. It is shown below that (i) these relations are moderately successful and (ii) the discrepancy which does occur is opposite to that expected for domain-wall relaxation effects.

Consider the internal energy of a magnetic material written

$$U = U_0 + U_m + \tfrac{1}{2} c_0 \epsilon^2 , \tag{1}$$

where subscripts 0 and m refer to nonmagnetic

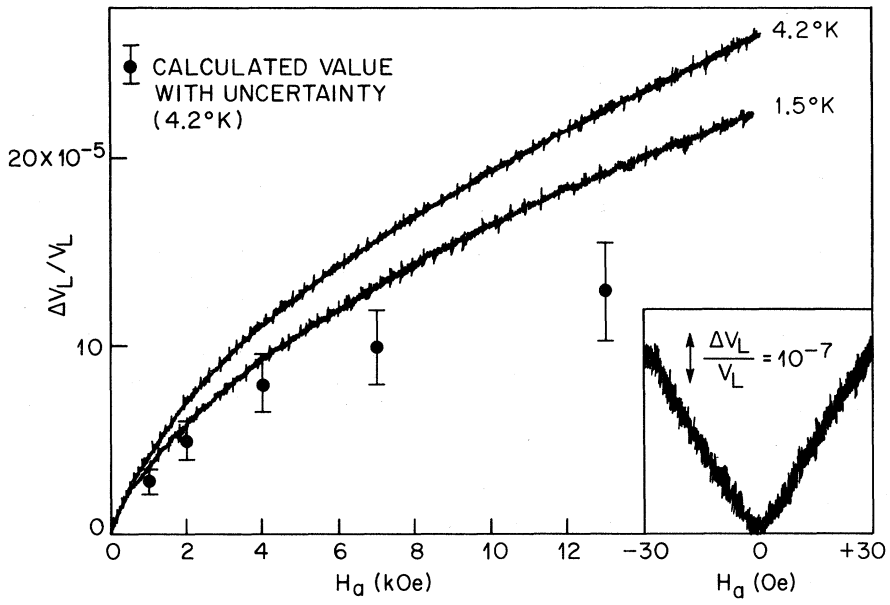

FIG. 4. Fractional change in longitudinal-wave sound velocity (20 MHz) vs applied field for Sc_3In. The insert shows data taken over a small-field range under quieter conditions. The indicated noise is representative. The reproducibility of the data is ~10%.

and magnetic contributions, respectively, U_0 is independent of strain, and c_0 is the adiabatic elastic modulus associated with strain ϵ. The elastic modulus $c = d^2U/d\epsilon^2 = \rho V^2$, where ρ is the mass density and V is the velocity of sound associated with strain ϵ. Since U_m, a function of magnetization M, is implicitly a function also of strain (via magnetostriction) one obtains

$$\frac{dU_m}{d\epsilon} = \frac{\partial U_m}{\partial M}\left|\frac{dM}{d\epsilon}\right|_{H_a} = H_a \left.\frac{dM}{d\epsilon}\right|_{H_a} = \left.\frac{cH_a d\epsilon}{dH_a}\right|_{\sigma},$$

where H_a is the applied field, σ is the stress, and the last equality is a Maxwell relation. All quantities are at constant entropy. Calculating the elastic modulus using the above formula (neglecting effects of order $d^2M/d\epsilon^2$) one finds the fractional change in sound velocity with applied field to be

$$\frac{\Delta[V]}{V} = \frac{\Delta[c]}{2c} = \frac{c\Delta}{2}\left[\left(\frac{d\epsilon}{dH_a}\right)_{\sigma}^2 \frac{dH_a}{dM}\right]$$

$$= \frac{c\Delta}{2}\left[\left(\frac{d\epsilon}{dM}\right)_{\sigma}^2 \frac{dM}{dH_a}\right], \qquad (2)$$

where $\Delta[x] = x(H_a) - x(0)$. {The fractional difference in sound velocity due to the term U_m at the same volume and temperature is given by Eq. (2) with $\Delta[x]$ replaced by x in the right-hand quantity. This behavior was not investigated in detail experimentally.}

Before comparing Eq. (2) with experiment, several corrections are usually necessary.[7] The isothermal values of $d\epsilon/dH_a$, $d\epsilon/dM$, and dM/dH_a, which are usually obtained experimentally, must be converted to the adiabatic values for use in Eq. (2). Estimates, made from measured quantities using thermodynamic relations,[8] show this difference to be less than 10%. Further, a correction for the volume dependence of c_0 (via magnetostriction ϵ_{ms}) must be made. This anharmonic correction is given by

$$\frac{\Delta V_{anh}}{V} = \frac{3}{2}\frac{d\ln c}{d\ln v}\,\epsilon_{ms},$$

where v is the volume. The quantity $d\ln c/d\ln v$ is not known but estimated to have the typical value ~ -1 and yields a correction which is also less than 10% of the observed magnitude. Finally, because of the longitudinal- and transverse-field isotropy of the sound-velocity results, the relative orientation of ϵ and H_a need not be considered. Presumably the magnetostriction is a simple volume effect in this polycrystalline sample.

To compare Eq. (2) with experiment, the magnetostriction results of Fawcett and Meincke[3] are given in Fig. 1. One finds a qualitative agreement between predicted and observed behaviors with the largest discrepancy at the higher fields (see Fig. 4). At 1.5 °K (predicted values not shown) the deviation is somewhat smaller than that found at 4.2 °K. This discrepancy may arise partly from sample inhomogeneity because of the critical dependence of the magnetic behavior on composition.[1] Neglect of higher-order magnetostrictive effects may also contribute some error. [The term $(H_a/2c)(d^2M/d\epsilon^2)_{H_a}$ neglected in the right-hand sides of Eq. (2) cannot be evaluated from available information.] The adiabatic-isothermal correction and the anharmonic correction, discussed above, will reduce the discrepancy by ~10%. The experimental error of 10% for the sound-velocity data is also to be considered.

Domain relaxation effects do not appear significant, as conjectured above, since these would cause the observed magnitude to be smaller than that predicted. Eddy currents should lead to domain-wall damping effects and a vanishing field dependence of the velocity of sound at frequencies such that the skin depth is less than the domain size.[9] The absence of these effects leads to the estimate (assuming an electrical resistivity $\rho \sim 50 \times 10^{-6}\ \Omega$ cm) that the domain size is less than ~10 μ.[10]

The behavior of shear waves in a magnetic field was found to be similar to that for longitudinal waves shown in Fig. 4 but with magnitude roughly 10% larger. Presumably a coupling exists between shear strain and magnetization in Sc_3In. (For example, these results could imply a change in magnetization with c/a ratio at constant volume for this hexagonal crystal.) No test of Eq. (2) is possible for the shear-wave data because of a lack of shear-magnetostriction data.

IV. SPECIFIC HEAT

Specific-heat data[11] in zero field and 1.3 kOe for this sample are shown in Fig. 5. The data show that at the reported[12] Curie point (≈ 7.5 °K) there is no anomaly although a small change in slope at 5.6 °K is evident on an expanded plot of c_p vs T. This is in contrast to the larger cusplike anomaly found by Isaacs and co-workers[11] also at a temperature of 5.6 °K. Our results may be due to a small inhomogeneity broadening of the transition temperature. However, at 4.2 °K and below (where most of our analyses are made) our sample showed the full magnetic moment reported by Gardner *et al.*[2] and by Isaacs and co-workers.[11]

Note that the 1.3-kOe-field data cross the zero-field data at 5.6 °K. This result can be predicted from thermodynamic arguments. The field dependence of the specific heat per mole c_p is given by the thermodynamic relation

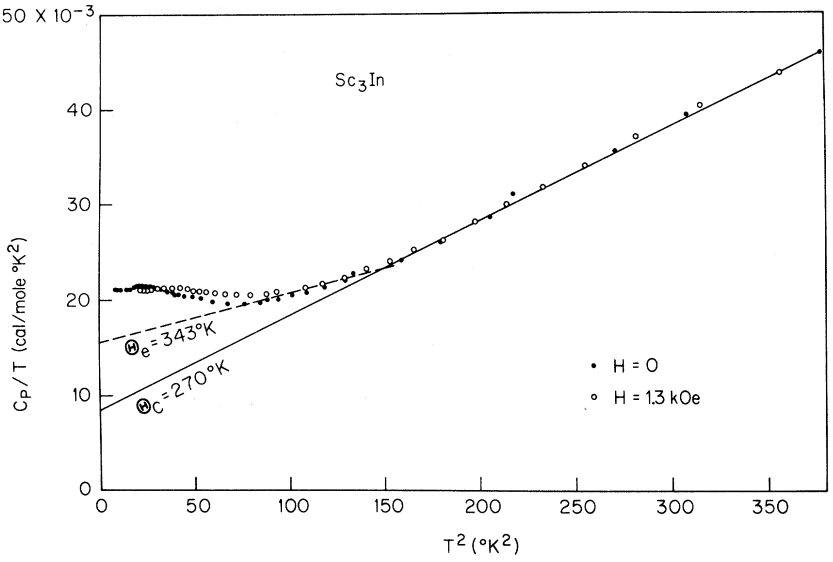

FIG. 5. c_p/T vs T^2. The dashed line shows the slope expected for the "elastic" Debye temperature. The difference between the zero field and 1.3 kOe data was reproducible below 13 °K but not above.

$$\left(\frac{dc_p}{dH_a}\right)_{T,\sigma} = Tv\left(\frac{d^2M}{dT^2}\right) , \qquad (3)$$

where v is the molar volume (≈ 57 cm^3 for Sc_3In). From measurements of M at six temperatures between 1.5 and 10 °K, we estimate, using Eq. (3), that the specific heat increases with an applied field of 1.3 kOe for $T \gtrsim 6$ °K. The largest calculated increase is for $T \sim 8$ to 9 °K and is $\sim 5\%$ in magnitude. At least for part of the range in temperature below 6 °K (less M-vs-T data are available here) the application of 1.3 kOe will reduce the specific heat by amounts $\sim (1-2)\%$. These results are in reasonable agreement with the experimental data shown in Fig. 5.

Analysis of the specific-heat data above 13 °K yields a Debye temperature $\Theta_c \approx 270$ °K and an electronic term $\gamma \approx 8\times10^{-3}$ cal/mole °K^2 (equivalent to 3.5 states of 1 spin/eV atom at the Fermi level). Using the longitudinal- and transverse-sound-velocity data for the polycrystalline sample to calculate an average velocity[13] for the Debye model yields $\Theta_e \approx 343 \pm 25$ °K for the limiting low-temperature behavior. The equivalent slope is shown by the dashed line in Fig. 5. The discrepancy between Θ_e and Θ_c probably arises because the calorimetric data are analyzed at temperatures too high to obtain the Debye behavior. The region between 13 and 19 °K, where c_p is proportional to T^3, is an accidental (but not unprecedented) behavior which may arise, in part, from the particular phonon dispersion. Below 13 °K the specific heat is complicated by the magnetic contribution.

ACKNOWLEDGMENTS

We wish to thank E. Corenzwit for sample preparation, E. Fawcett for helpful discussions as well as the magnetostriction data, G. Knapp for communicating his specific-heat data to us prior to publication, and William Royer for technical assistance.

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[3]E. Fawcett and P. P. M. Meincke, J. Phys. (Paris) 32, Colloq. 1, C1-629 (1971).

[4]Magnetization measurements of this sample were also made by R. C. Sherwood.

[5]This susceptibility value has an uncertainty of $\sim 10\%$ due to a small demagnetizing-factor uncertainty. At $T = 4.2$ °K the initial susceptibility was $\sim 10\%$ less with still essentially no remanence, coercive field, or hysteresis.

[6]This behavior resembles that of superparamagnetism. However, the magnetization at different temperatures when plotted against H/T does not fall on a single universal curve as expected for superparamagnetism. Corrections for the temperature dependence of the spontaneous moment would increase the discrepancy with the expected universal curve. See I. S. Jacobs and C. P. Bean, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1963), Vol. III, p. 277.

[7]Since the field dependence of the velocity of sound is independent of the angle between propagation and field directions, no magnetohydrodynamic effect of the type described by R. A. Alpher and R. J. Rubin [J. Acoust. Soc. Am. 26, 452 (1954)] need be considered.

[8]The fractional adiabatic-isothermal difference

$$\frac{x_s - x_T}{x_T} = -Tv\left(\frac{dM}{dT}\right)^2 \Big/ c_p\left(\frac{dM}{dH}\right) \quad \text{for } x = \frac{dM}{dH}$$

$$= -\alpha T v \left(\frac{dM}{dT}\right)\left(\frac{dH}{d\epsilon}\right)\Big/ c_p \quad \text{for } x = \frac{d\epsilon}{dH}.$$

α is the linear thermal-expansion coefficient, c_p is the specific heat per mole, and v is the molar volume (≈ 57 cm^3 for Sc_3In).

[9]W. P. Mason, Phys. Rev. 83, 683 (1951); see also L. R. Testardi and J. H. Condon, Phys. Rev. B 1, 3928 (1970).

[10]This behavior and the observed isotropy with respect to field and propagation directions are also consistent with the superparamagnetic state (but see Ref. 6).

[11]Specific-heat data for Sc_3In below 4 °K have recently been reported by L. L. Issacs and G. S. Knapp, Bull. Am. Phys. Soc. 15, 1623 (1970). More detailed data are given by L. L. Isaaxa, G. S. Knapp, and H. V. Culbert (unpublished).

[12]This is the Curie temperature reported by Gardner *et al.* (Ref. 2) and defined as the temperature where a spontaneous moment (obtained by extrapolation from $H > 1$ kOe) should occur. A value of 6.1 °K was obtained by these authors using initial susceptibility data.

[13]This approximation is usually good to better than 10%. It fails in the rare case of large selective acoustic mode softening and damping.

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Magnetothermal Properties of Heat Transport in Cobalt Chloride Thiourea*

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Thermal-conductivity measurements have been made on a single crystal of cobalt chloride thiourea, $CoCl_2 \cdot [(NH_2)CS]_4$, in the temperature range 0.35–20 K and in applied magnetic fields of up to 20 kG. Below the Néel temperature of 0.92 K, an enhancement in conductivity for heat flowing in the [001] sublattice-magnetization direction is interpreted as due to the onset of spin-wave conductivity. Data taken for heat flowing in a normal [110] direction show no such enhancement. Relatively sharp changes in the conductivity as a function of temperature and magnetic field have been used to obtain information on the paramagnetic-antiferromagnetic and antiferromagnetic–spin-flop phase boundaries. Magneto-thermal-resistance resonances in the paramagnetic state have yielded information on the magnitude and anisotropy of the g value for the unpaired electronic state of the cobalt ion.

I. INTRODUCTION

At low temperatures, the statistical properties of a physical system are determined by the low-lying excitations of the system. Spin-wave theory has been recognized as providing a successful model for studying magnetic substances in this regime. In an antiferromagnet, the magnetic ions are (super)exchange coupled to their neighbors in such a way that the long-range ordering which occurs below the Néel temperature (T_N) leads to a spontaneous magnetization. Antiferromagnetic spin waves are generated from an ordered array of alternately pointing spins, which on the basis of Anderson's calculation[1] for the antiparallel-spin-sublattice model is a reasonable approximation of its ground state. Experimental evidence for the excitation of antiferromagnetic spin waves of definite wave vector has been observed in antiferromagnetic resonance measurements for $q = 0$ by Jacobs *et al.*[2] and others,[3,4] and from neutron-inelastic-scattering measurements for $q \neq 0$ by Okazaki *et al.*[5] Such collective excitations could transport energy at low temperatures provided $T < T_N$. It was first speculated by Sato[6] that it may be of interest to measure the thermal conductivity of an antiferromagnet. Since then, antiferromagnetic–spin-wave heat-transport observations were attempted in a variety of antiferromagnetic insulators by Slack,[7] by Donaldson and Edmonds,[8] and by Gorter and Tinbergen.[9] However, positive identification of spin-wave thermal-energy transport has not been made in the investigated insulating systems.

A preliminary report by Weinstock[10] (on two crystals other than those used in the current study) indicated that there might be a possible antiferromagnetic–spin-wave contribution to the thermal conductivity of antiferromagnetic cobalt chloride thiourea. Some useful physical properties of this crystal are summarized in the Appendix.

This particular crystal system appears to be a good one for attempting to identify antiferromagnetic–spin-wave heat transport. It is a uniaxial two-sublattice system, with its spontaneous-magnetization direction along the [001] direction. For such a relatively simple magnetic structure, theoretical analysis is available.

Another important feature is that the Néel temperature is much lower than the Debye temperature, i.e., $T_N \ll \Theta_D$. The Néel temperature has been determined by both heat-capacity[11] and susceptibility[12] measurements to be 0.92 K, while the same heat-capacity work carried to higher temperature yields $\Theta_D \approx 65$ K. These heat-capacity