The Variation of the Adiabatic and Isothermal Elastic Moduli and Coefficient of Thermal Expansion with Temperature through the λ-Point Transition in Ammonium Chloride*

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Measurements of the temperature variation of the adiabatic and isothermal Young's and rigidity moduli and of the coefficient of thermal expansion of pressed specimens of ammonium chloride in the neighborhood of the λ-point transition at 242.8°K are reported. It is found that a large difference exists between the adiabatic and isothermal compressibilities below the critical temperature, and hence a large difference between the specific heat at constant pressure and the specific heat at constant volume. The data, in conjunction with the known temperature variation of the specific heat at constant pressure, permit the evaluation of the temperature variation of the specific heat at constant volume, and from this it is concluded that the transition is not to be associated, as previously suggested by Pauling, with the occurrence of almost free rotation of the ammonium radicals in the crystal lattice.

INTRODUCTION

THE crystalline structure of ammonium chloride is cubic.[1] The chlorine atoms lie at the vertices of the elementary cubes and the nitrogen atoms at the centers. Four hydrogen atoms form a tetrahedral array about each nitrogen atom and, at low temperatures at least, there appears to be a common preferred orientation for all the tetrahedra in the crystal, *viz.* one in which a symmetry axis of the tetrahedron lies parallel to a diagonal axis of the cube.[2]

Many physical properties of ammonium chloride vary sharply but continuously with temperature in the neighborhood of 242.8°K. Thus, as the temperature is raised through an interval of only a few degrees, the specific heat at constant pressure[3] and coefficient of thermal expansion[4] increase many times in value and then decrease; the substance ceases to be piezoelectric;[5] the dielectric constant and dielectric absorption increase;[2] there is a shift in the characteristic infra-red absorption frequencies;[6] and a change in the Raman spectrum.[2]

Now x-ray analysis reveals no change in the lattice structure in this critical temperature interval,[7] hence the foregoing phenomena must be associated in some manner with the behavior of the hydrogen tetrahedra: for the light hydrogen atoms alone leave no trace of their presence on the x-ray record. The object of the present research is to obtain further data upon which to base a study of this behavior. In particular, it is desired to know the way in which the specific heat at constant volume varies with temperature during the transition.

The specific heats at constant pressure and constant volume are related by the formula

$$c_p - c_v = Tv\alpha^2/\kappa_t, \tag{1}$$

in which c_p and c_v denote, respectively, the two molal specific heats, T the absolute temperature, v the molal volume, α the volume coefficient of thermal expansion, and κ_t the isothermal compressibility. It is proposed to calculate c_v by inserting measured values of the remaining quantities in this formula, but it must be remarked that, in virtue of its origin, Eq. (1) is directly applicable only to *reversible* processes,

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[1] G. Bartlett and I. Langmuir, J. Am. Chem. Soc. **43**, 84 (1921); R. Wyckoff, Am. J. Sci. **3**, 177 (1922); **4**, 193 (1922).

[2] A. C. Menzies and H. R. Mills, Proc. Roy. Soc. **A148**, 407 (1935).

[3] Simon, von Simson and Ruheman, Zeits. f. physik. Chemie **A129**, 339 (1927).

[4] F. Simon and R. Bergman, Zeits. f. physik. Chemie **B8**, 255 (1930); A. Smits and G. H. MacGillavry, Zeits. f. physik. Chemie **A166**, 97 (1933); H. Adenstedt, Ann. d. Physik **26**, 69 (1936).

[5] S. Bahrs and J. Engl, Zeits. f. Physik **105**, 470 (1937).

[6] A. Hettner and F. Simon, Zeits. f. physik. Chemie **B1**, 293 (1928); A. G. Pohlmann, Zeits. f. Physik **79**, 394 (1932).

[7] F. Simon and C. von Simpson, Naturwiss. **14**, 880 (1926); J. A. Ketelaar, Nature **134**, 250 (1934).

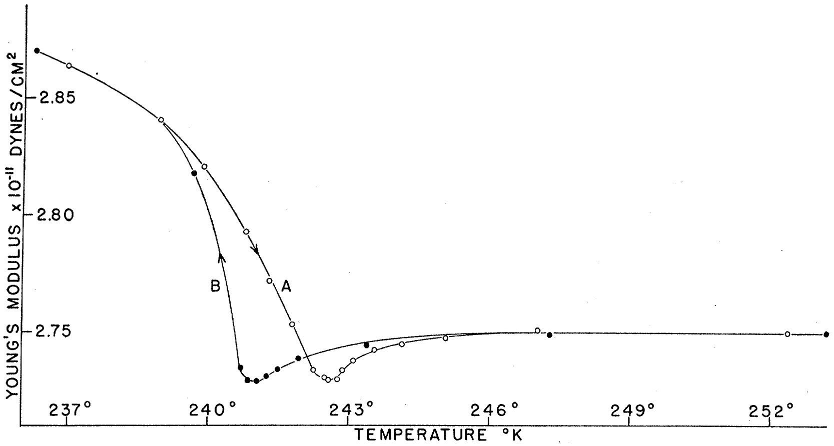

FIG. 1. The way in which the adiabatic Young's modulus varies with temperature near the transition when the material is (A) heated, and (B) cooled.

that is, to processes during which the state of the system, as determined by specific values of the thermodynamic coordinates, does not depend upon the previous history of the system. In this sense the processes here under review are not reversible, for it is known that the values of α and κ at a given temperature in the transition region depend upon whether the material has been brought to that temperature by heating it or by cooling it. The nature of this phenomenon is illustrated by the curves of Fig. 1, in which the quantity dealt with is the adiabatic Young's modulus. Accordingly, the validity of Eq. (1) is subject to question when T lies in the transition interval. It is proposed to resolve this question in the following manner:

The isothermal and adiabatic compressibilities of a substance are related by the formula

$$\kappa_t - \kappa_s = Tv\alpha^2/c_p, \tag{2}$$

in which κ_s denotes the adiabatic compressibility, and this equation is subject in the same manner to the same condition concerning reversibility as is Eq. (1), for both follow from the two fundamental thermodynamic formulae known[8] as the "$T\,dS$ equations." If, therefore, the validity of Eq. (2) over the transition interval can be established experimentally, then that of Eq. (1) may be accepted without demur.

The compressibility of an isotropic material is related to the Young's and rigidity moduli by the formula

$$\kappa = (9/E) - (3/\mu), \tag{3}$$

where E and μ denote, respectively, the Young's modulus and the rigidity modulus. The adiabatic and isothermal values of the latter are identical, since pure torsion involves no change in volume. Hence, for the purpose of the preceding argument, Eq. (2) may be replaced by the equation

$$(9/E_t) - (9/E_s) = Tv\alpha^2/c_p. \tag{4}$$

The experimental verification of this formula requires the measurement of the variations of E_t, E_s, α and c_p with temperature on a homogeneous, isotropic specimen. The variation of c_p with temperature through the transition has been measured by Simon, von Simson and Ruheman,[3] and their data are used in the calculations which follow. The experiments here reported are concerned with E_t, E_s, μ and α.

EXPERIMENTAL METHODS

The adiabatic moduli

A complete description of the dynamical method employed for measuring the adiabatic Young's and rigidity moduli has appeared in previous issues of this journal.[9] Accordingly it will suffice here briefly to review its essential features. The specimen is in the form of a right circular cylinder 4.7 cm in diameter and a few

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[8] See, for example, M. Zemansky, *Heat and Thermodynamics* (McGraw-Hill, 1937), p. 225.

[9] L. Balamuth, Phys. Rev. **45**, 715 (1934); M. E. Rose, Phys. Rev. **49**, 50 (1936); M. A. Durand, Phys. Rev. **50**, 449 (1936).

centimeters long. The required data are deduced from the observed behavior of a separately excited composite piezoelectric oscillator constructed by cementing to one end of the specimen a suitably cut cylinder of crystalline quartz of identical cross section. Silver electrodes are deposited in proper position on the quartz, and the oscillator is suspended vertically by delicate supports attached at the middle of the quartz cylinder. The fundamental frequency of free longitudinal or torsional vibration of this system is measured by observing the variation of the electrical impedance of the composite oscillator with the frequency of the applied voltage, and from this the frequency, f, of free longitudinal or torsional vibration of the specimen cylinder alone is calculated. The latter quantities are related, respectively, to E_s and μ by the formula

$$2fL=(M/\rho)^{\frac{1}{2}}, \tag{5}$$

where L is the length of the specimen cylinder, ρ the density, and M the elastic modulus.

Thermal expansion

The coefficient of thermal expansion is obtained by graphical differentiation of a linear thermal expansion curve plotted from data taken with the simple form of dilatometer described by Siegel and Quimby.[10] The change in length of a specimen 4 cm long can be measured with an accuracy of 0.001 mm, and the consequent uncertainty in the normal value of α is 1 percent.

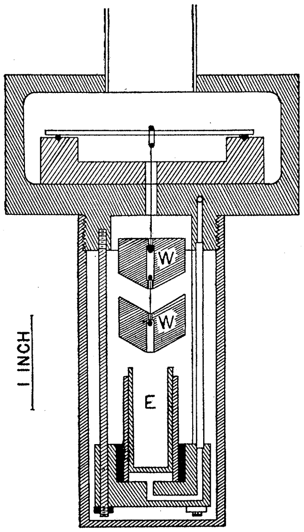

FIG. 2a. Cross-sectional diagram of the apparatus for measuring the temperature variation of the isothermal Young's modulus, showing the mounted specimen, weights and hydraulic elevator.

Isothermal moduli

The adiabatic and isothermal values of Young's modulus differ by less than 2 percent at temperatures removed from the transition region. Furthermore, the adiabatic modulus can be measured, by the method outlined above, with far greater accuracy than can the isothermal modulus. Thus, *at any temperature removed from the transition*, a better value of E_t can be obtained from the corresponding value of E_s with the aid of Eq. (4), than can be obtained by direct measurement. Accordingly, the apparatus about to be described is designed only to measure the *ratio* of the value of E_t at a fixed temperature to that at any other temperature.

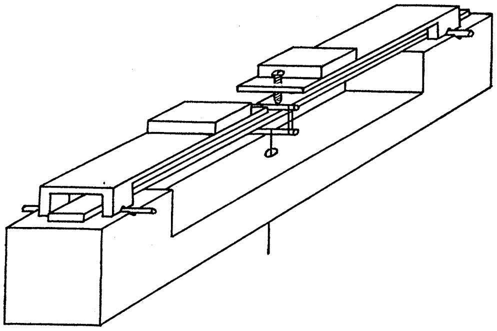

FIG. 2b. Detailed diagram of specimen mount, showing lever and mirror system.

Figure 2 is a schematic diagram of the apparatus. The specimen, in the form of a rectangular beam 6 cm long by 4 mm wide by 1.5 mm thick, rests horizontally on two smooth fused quartz rods 1 mm in diameter and 5 cm apart. The specimen is bent by two Duralumin weights hung from a centrally located stirrup, and applied singly by lowering a hydraulic elevator constructed from parts of a glass hypodermic syringe. The elevator liquid is methanol, and the operation is effected by manipulation of a duplicate syringe in fluid connection with the first. The amount of bending of the specimen is measured by observing the relative angular

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[10] S. Siegel and S. L. Quimby, Phys. Rev. **54**, 76 (1938).

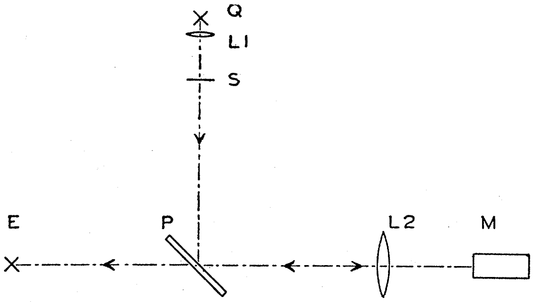

FIG. 3. The optical system for measuring the amount of bending of the specimen.

deflection of two light beams reflected one from each of two small horizontal mirrors attached to two levers. One end of each lever rests on the specimen at a point near its center, and the other end pivots on one of the quartz rods which support the specimen.

The specimen and the associated lever system are mounted in a stout, sealed copper box, which is supported, through a one-inch copper to glass seal, by a vertical glass tube. The incident and emerging light beams pass through this tube. The entire apparatus is immersed in the cryostatic bath described below.

Figure 3 is a plan diagram of the remainder of the optical system employed to measure the beam deflection. Light from a strip filament lamp, Q, is focused on a horizontal slit, S, which is a focal length distant from a lens, L_2. Light emerging from the slit is, in part, reflected through L_2 by a plate glass mirror, P, is rendered parallel by L_2, and reflected downward onto the lever mirrors by a silvered mirror, M. The returning beams of parallel light are reflected back by the mirror M through the lens L_2, which forms two images of the slit in the focal plane of a filar micrometer eyepiece, E. When the specimen beam is bent, these two images separate, and the amount of this separation, as measured by the filar micrometer, is proportional to the downward displacement of the center of the beam.

The focal length of the lens L_1 is 4 cm, and that of L_2 is 115 cm. The minimum observable displacement of the beam center is 10^{-5} cm. Proportionality between stress and strain in the material is verified at each temperature by comparison of the displacements produced, respectively, by one and both of the weights.

Internal friction

The experimental method, described above, for measuring the adiabatic elastic moduli yields at the same time values of the coefficients of internal friction of the substance.[11] These quantities are associated with the types of normal vibration of a body, and are defined, one for each type, as the coefficient of the vibrational stress amplitude squared in the expression for the energy dissipated per unit volume per cycle of vibration.[12] They thus resemble the elastic moduli in that their definition requires the specification of a stress. The types of stress here dealt with are the stretch and twist associated, respectively, with the longitudinal and torsional vibration of a slender bar.

Temperature control

Observations of E_s, E_t, μ and α are made with the specimen, enclosed in the appropriate envelope, immersed in a well-stirred methanol bath contained in a large Dewar vessel. This liquid is cooled by a continuous circulation of cold methanol through a pair of copper coils, one of which is immersed in the bath and the other in a solution of carbon dioxide snow and methanol. The circulation is maintained by a centrifugal pump, which is itself immersed in the solution. The temperature of the bath is kept constant to 0.01°K by adjusting the flow of the cooling liquid, and also the power dissipated in a quick acting electric immersion heater located in the bath.

The temperature is measured with a platinum resistance thermometer, used in connection with a Mueller bridge. The thermometer calibration is certified by the National Bureau of Standards, and is checked at the melting point of ice and the boiling point of a quantity of oxygen which has stood in a Dewar vessel for a week.

RESULTS

Specimen material

The ideal specimen material for an investigation of the lattice properties of a solid is, of course, a single crystal. Natural crystals of ammonium chloride occur in lava deposits, but

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[11] S. Siegel and S. L. Quimby, Phys. Rev. **49**, 663 (1936).
[12] W. T. Cooke, Phys. Rev. **50**, 1158 (1936).

are small and very impure. Unsuccessful attempts were made to grow single crystals by slow cooling from the molten material,[13] and by slow crystallization from a saturated solution containing pectic acid.[14] Crystals formed by the first method were shattered by the large change in volume which accompanies the crystallographic transformation at 186°C, and the second method failed to produce crystals of adequate size or structural perfection. It will be noted, however, that to obtain the data here sought, namely the temperature variations of c_v, α and κ, it is not necessary to use a single crystal, and the foregoing difficulties discouraged further attempts to secure one.

Polycrystalline specimens are cut from a block of material prepared by compressing dry granulated ammonium chloride[15] to 50,000 lb./in.^{2} in a steel cylinder at room temperature. The result is a coherent array of microcrystals whose average linear dimension, as revealed by photomicrographs, is 5×10^{-3} cm. Experiments made on specimen cylinders cut along different directions in the block reveal no trace of anisotropy. The densities of different blocks at 24°C vary slightly about the value 1.520 g/cm^3, which is slightly less than the density of crystalline ammonium chloride as measured by Wulf and Cameron,[16] namely 1.527 g/cm^3.

TABLE I. *The variation of the thermal expansion of polycrystalline ammonium chloride with temperature.*

T °K	$\Delta L/L$ $\times 100$	α $\times 10^4$	T °K	$\Delta L/L$ $\times 100$	α $\times 10^4$
224.0	0.593	1.70	242.5	0.325	23.3
228.0	.562	2.64	242.6	.313	29.4
232.0	.523	3.28	242.7	.294	51.0
235.0	.487	3.85	242.8	.261	183.
237.0	.461	4.17	242.9	.218	103.
238.0	.446	4.65	243.0	.184	38.8
239.0	.430	5.12	243.1	.178	14.3
240.0	.411	6.42	243.2	.174	7.40
241.0	.388	8.00	243.5	.168	3.56
241.6	.370	10.4	244.5	.161	2.00
241.9	.359	12.1	246.0	.152	1.89
242.1	.351	14.3	249.0	.133	1.86
242.2	.346	16.0	255.0	.095	1.83
242.3	.340	18.1	263.0	.049	1.67
242.4	.333	20.5	273.2	.000	1.23

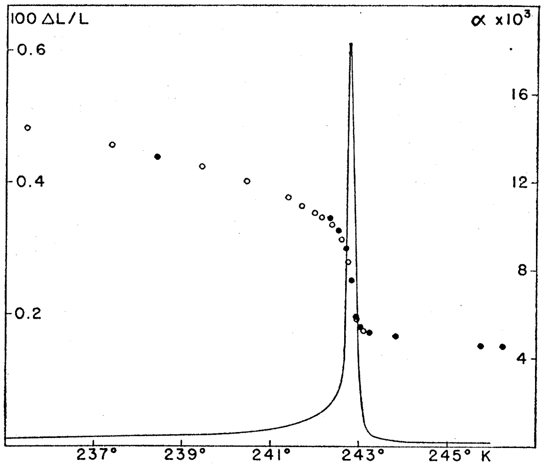

FIG. 4. The thermal contraction curve and the variation of the volume coefficient of thermal expansion with temperature near the transition.

Except as otherwise specified, the measurements which follow were all made on specimens whose density is 1.520 g/cm^3, and all were made as the temperature of the specimen was progressively *raised.*

Thermal expansion

The observed linear thermal expansion of two specimens of ammonium chloride between 236°K and 247°K is plotted in Fig. 4. The curve in this figure shows the variation of the volume coefficient of thermal expansion with temperature, the ordinates being three times the slope of a smooth curve drawn through the plotted $\Delta L/L$ data. The maximum value of α occurs at the temperature 242.8°K. Corresponding data over the temperature range 224°K to 273°K are given in Table I.

The thermal expansion of a pressed specimen whose density is 1.512 g/cm^3 is indistinguishable by the present experimental method from that of a specimen whose density is 1.520 g/cm^3.

Adiabatic elastic moduli

The variations of the adiabatic Young's modulus, rigidity modulus, compressibility, and Poisson's ratio with temperature over the transition interval are shown in Figs. 5 and 6. The compressibility, κ_s, is calculated from the observed E_s and μ with Eq. (3), and Poisson's ratio, σ_s, with the formula

$$\sigma_s = (E_s/2\mu) - 1. \tag{6}$$

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[13] H. Rassow, Zeits. f. anorg. allgem. Chemie **114**, 117 (1920).

[14] F. Ehrlich, Zeits. f. angew. allgem. Chemie **203**, 26 (1931).

[15] Eimer and Amend Company, New York, Tested Purity Reagent.

[16] P. Wulff and H. K. Cameron, Zeits. f. physik. Chemie **B10**, 347 (1930).

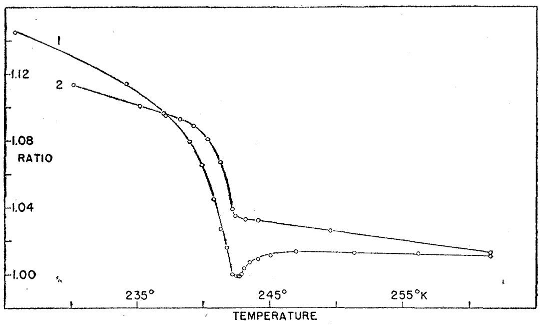

FIG. 5. The variation of the adiabatic Young's modulus (curve 1) and rigidity modulus (curve 2) with temperature near the transition point. The ordinates are the ratios of the values at the given temperature to the values at 273.2°K.

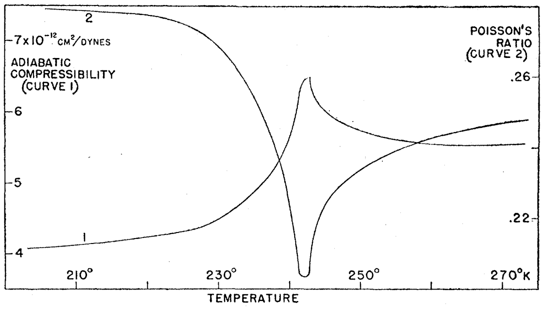

FIG. 6. The variation of the adiabatic compressibility (curve 1) and Poisson's ratio (curve 2) with temperature.

Complete data over the temperature interval 205°K to 273°K are presented in Table II. The second column of this table contains values of E_s measured at the temperatures given in the first column. The corresponding values of μ, which appear in the third column, are obtained from the measured values of this quantity by graphical interpolation. The remaining columns are calculated with Eqs. (3) and (6). It will be noted that the maximum value of the compressibility and the minimum values of Young's modulus and Poisson's ratio occur at the temperature 242.8°K.

The isothermal compressibility of the present specimens of ammonium chloride, computed from the data of Tables I and II with the aid of Eq. (2), is 5.64×10^{-12} cm²/dyne at 0°C. The only other measurement of this quantity of which the writer is aware is that of Bridgman,[17] who worked with polycrystalline specimens pressed at about 310,000 lb./in.². The density of these specimens is not reported. Bridgman's experiments lead to the value 5.60×10^{-12} cm²/dyne.[18] It must not, however, be assumed that either of these values is characteristic of the crystal lattice. Indeed, it is found that the compressibility of a pressed specimen depends to a marked degree upon its density. Thus the isothermal compressibility of a specimen whose density is 1.512 g/cm³ is 6.7 percent greater than that of a specimen whose density is 1.520 g/cm³. A cognate example of the discordance between observations made on single and polycrystalline specimens is found in magnesium oxide, for which the observed compressibility of a single crystal is 0.59×10^{-6} cm²/kg, while that of a pressed specimen is 0.99×10^{-6} cm²/kg.[19]

It is further found, however, that small changes in density are very nearly without effect on the *temperature variations* of the elastic moduli, expressed in percent change per degree. For example, the ratios of the values of the compressibilities at 220°K to those at 273°K for the two specimens cited above differ by only 1.2 percent, the less dense specimen having the larger ratio.

Isothermal elastic moduli

The variation of the isothermal Young's modulus with temperature through the transition interval is given in Table III. The second column of this table contains values of the ratios E_t^0/E_t, where E_t^0 denotes the value of the modulus at 235.73°K and E_t that at the temperature indicated in the first column. This ratio is related to the observed ratio of the corresponding beam displacements, y^0/y, by the formula

$$E_t^0/E_t=(y/y^0)(1+4\delta_L), \qquad (7)$$

where δ_L denotes the change in length per unit length of the specimen material between 235.73°K and the temperature of observation. The correction term in this formula represents the effect of lateral thermal expansion on the stiffness of the beam.

The value of E_t^0 used in computing the data given in the third column of Table III is calculated, as before mentioned, from the observed value of E_s at 235.73°K with Eq. (4).

It is found that ammonium chloride is plastic over a temperature interval of about 0.3°K at the

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[17] P. W. Bridgman, Phys. Rev. **38**, 182 (1931).

[18] A. May, Phys. Rev. **52**, 339 (1937).

[19] P. W. Bridgman, Proc. Am. Acad. Sci. **67**, 345 (1932).

transition, and it is therefore impossible to measure E_t at temperatures which lie in this range. The beam displacement increases steadily with time after the load is applied, at such a rate that the increase in 5 minutes is about half the initial displacement. This plasticity disappears immediately above and immediately below the transition temperature. Copper-gold alloys[20] and quartz[21] have been shown to behave in a similar manner at their transition temperatures.

It will be recalled that the object of the isothermal measurements is to establish the validity of Eq. (4) in the transition interval. The affirmative nature of the result is indicated in Fig. 7. The points plotted in this figure indicate the *observed* values of the ratio E_t^0/E_t, and the smooth curve values *calculated* with Eq. (4) from the data given in Tables I and II, together with those on c_p obtained by Simon, von Simson and Ruheman.[3] The hiatus left in this curve signifies the uncertainty, admitted by the last named investigators, in their values of c_p immediately at and immediately above the transition temperature.

TABLE II. *The variation of the adiabatic elastic moduli of polycrystalline ammonium chloride with temperature.*

T °K	$E_s\times10^{-11}$ DYNES/CM^2	$\mu\times10^{-11}$ DYNES/CM^2	$\kappa_s\times10^{11}$ CM^2/DYNES	σ_s
205.42	3.2372	1.2633	0.406	0.281
216.27	3.1832	1.2445	.417	.279
225.72	3.1286	1.2280	.434	.274
234.18	3.0462	1.2119	.479	.258
236.92	2.9975	1.2034	.510	.245
238.94	2.9492	1.1948	.541	.234
239.87	2.9134	1.1886	.565	.226
240.81	2.8567	1.1770	.602	.214
241.32	2.8220	1.1656	.615	.211
241.79	2.7777	1.1502	.632	.207
242.25	2.7378	1.1375	.650	.203
242.50	2.7319	1.1343	.650	.204
242.59	2.7300	1.1337	.651	.204
242.75	2.7299	1.1331	.649	.204
242.87	2.7377	1.1329	.649	.208
243.10	2.7461	1.1327	.629	.212
243.52	2.7546	1.1322	.618	.216
244.15	2.7610	1.1314	.608	.220
245.08	2.7668	1.1301	.598	.224
247.04	2.7721	1.1274	.586	.229
251.38	2.7696	1.1223	.577	.234
256.21	2.7684	1.1165	.564	.240
261.61	2.7635	1.1100	.554	.245
273.18	2.7316	1.0953	.556	.247

Internal friction

The way in which the internal friction associated with longitudinal vibration of the specimen cylinders varies with temperature is shown in Fig. 8. The torsional internal friction behaves in a similar manner.[22] Little of a quantitative nature can be written concerning this phenomenon at the present state of development of the theory. The high internal friction at the transition is, of course, associated with the observed plasticity of the material at this temperature. Again, the thermoelastic theory of Zener[23] indicates that the total internal friction contains a part proportional to c_p-c_v, and it will be seen that the value of the latter quantity becomes very large at the transition temperature.

TABLE III. *The variation of the isothermal Young's modulus of polycrystalline ammonium chloride with temperature.*

T °K	E_t^0/E_t	$E_t\times10^{-11}$ DYNES/CM^2	T °K	E_t^0/E_t	$E_t\times10^{-11}$ DYNES/CM^2
228.71	0.956	3.034	241.97	1.284	2.259
235.73	1.000	2.901	242.24	1.410	2.057
237.58	1.034	2.830	242.39	1.589	1.826
238.90	1.035	2.763	242.48	1.788	1.622
239.53	1.085	2.706	243.08	1.113	2.606
240.51	1.098	2.625	243.33	1.095	2.649
240.81	1.112	2.583	243.82	1.084	2.676
241.47	1.185	2.452	244.31	1.078	2.691
241.87	1.235	2.338	245.28	1.066	2.721

Specific heat at constant volume

The difference c_p-c_v is evaluated with Eqs. (1) and (2), from the observed values of α, κ_s and c_p by eliminating κ_t between the two equations, and the value of c_v then follows. The result is shown in Fig. 9, in which the circles are a plot of Simon, von Simson and Ruheman's data and the dots are the calculated values of c_v. The latter quantities appear in the last column of Table IV. The estimated uncertainty in the quantity c_p-c_v increases from 0.2 cal./mol-deg. at 236°K to 2 cal./mol-deg. at 242.4°K.

Two questions arise in connection with the foregoing procedure, since this requires the combination of data obtained by different observers working with different specimens. The first is concerned with the value of c_p, but the writer can

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[20] W. S. Gorsky, Physik. Zeits. Sowjetunion **8**, 562 (1935).

[21] A. Perrier and R. de Mandrot, Mem. Soc. Vaud. **1**, 333 (1924).

[22] The internal friction of β-brass likewise is large at the transition; see Koster, Zeits. f. Electrochem. **45**, 30 (1939).

[23] C. Zener, Phys. Rev. **53**, 90 (1938).

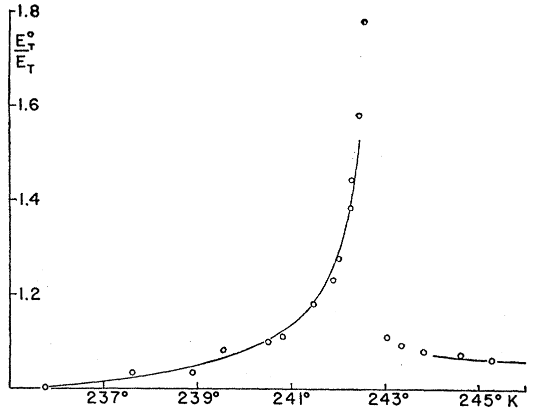

FIG. 7. Comparison of the observed ratios of the values of the isothermal Young's modulus at different temperatures (the circles), with those computed from the corresponding values of the adiabatic modulus with Eq. (4) (the curve).

adduce no reason why this quantity should depend upon the nature of the specimen. It appears that the value of c_p must be the same, whether measured on a pressed specimen, a powder, or a single crystal, provided only that large internal stresses do not exist. The absence of such stresses is indicated by the reproducibility of measurements made on successive traversals of the transition temperature, at which the material is plastic. The second is concerned with the identity of the two temperature scales employed. The fact that Simon and his co-workers found the maximum values of c_p and α at the same temperature, 242.8°K, as that here found for the occurrence of the maximum values of κ_s, α and the coefficient of internal friction, and the minimum value of E_s, indicates that the two temperature scales coincide with a somewhat surprising precision.

Still a third question is concerned with the meaning of c_v in connection with a pressed specimen whose density is less than that of a single crystal. The result of the isothermal measurements proves that there is, associated with a pressed specimen, a quantity which plays the role of c_v in the (correct) description of the behavior of the specimen offered by Eq. (1). The question is, how much will the value of this quantity differ from that which would be obtained from measurements made on a single crystal? An answer is suggested by comparison of the preceding data with the result of a duplicate set of measurements made on a pressed specimen whose density, 1.512 g/cm³, differs from that of the first specimen, 1.520 g/cm³, by about the same amount that the latter differs from that of a single crystal. The values of $c_p - c_v$ obtained from both specimens are presented for comparison in Table IV. It will be noticed that the indicated difference between corresponding values of c_v is not more than 1 cal./mol-deg., and is in the direction which would be expected, i.e.,

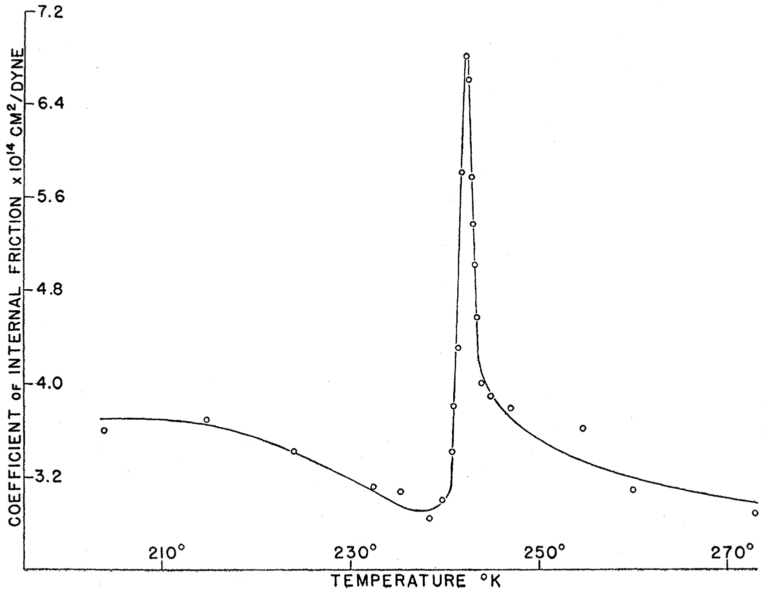

FIG. 8. Variation of the longitudinal internal friction with temperature in polycrystalline ammonium chloride.

c_v is larger for the less dense specimen. It is therefore concluded that the maximum value of c_v yielded by the denser specimen is, perhaps, one or two cal./mol-deg. larger than that which would be obtained from measurements made on a single crystal.

The uncertainty, mentioned above, in the values of c_p immediately at and immediately above the transition temperature discourages an attempt to calculate c_v in this interval. Indeed, unpublished data kindly supplied the writer by Dr. Ziegler of Johns Hopkins University[24] indicate that the values of c_p plotted on the dotted portion of the curve of Fig. 9 may be appreciably too high. It may be remarked that experiments designed to resolve this uncertainty are now in progress in this laboratory.

Two significant observations are suggested by a scrutiny of Fig. 9. The first is the large difference between c_p and c_v near the transition. This requires that any theory, such as that of Fowler,[25] which offers a description of the temperature variation of c_v through the transition must be compared with the observed variation of *this* quantity, and not, as has been done, with that of c_p.

The second concerns the value of c_v just above the transition, which is 18 cal./mol-deg. Of this amount, 12 cal./mol-deg. represents energy associated with the normal vibrations of the ammonium chloride lattice, and the remaining 6 cal./mol-deg. energy associated with the tetrahedral arrays of hydrogen atoms described at the beginning of this article. In accordance with classical statistical mechanics, the latter quantity is to be reckoned at the rate of 1 cal./mol-deg. for each quadratic term in the Lagrangian function of a tetrahedron, considered as a unit.[26] Now the theory of Fowler, cited in the preceding paragraph, is based upon the hypothesis, due to Pauling,[27] that at temperatures above the transition point the hydrogen tetrahedra rotate freely in the lattice, and that the inception of this free rotation is responsible for the phenomena here under review. This hypothesis, however, now seems untenable, since it implies a contribution, on the part of the tetrahedra, of three cal./mol-deg. to the specific heat instead of six.

TABLE IV. *Values of c_p-c_v obtained from measurements made on pressed specimens of different density; and the variation of c_v with temperature through the transition in ammonium chloride.*

T °K	c_p-c_v CAL./MOL-DEG. $\rho=1.512$ G/CM^3	c_p-c_v CAL./MOL-DEG. $\rho=1.520$ G/CM^3	c_v CAL./MOL-DEG. $\rho=1.520$ G/CM^3
236.0	4.7	5.0	19.8
237.0	5.0	5.4	20.0
238.0	5.9	6.2	20.1
239.0	6.8	7.2	21.1
240.0	9.3	9.8	21.3
241.0	13.0	13.2	21.9
241.5	16.5	17.1	21.2
242.0	23.8	24.8	21.2
242.2	31.0	31.1	21.4
242.4	42.5	43.5	21.5
245.0	1.7	1.8	20.2
246.0	1.1	1.2	19.2

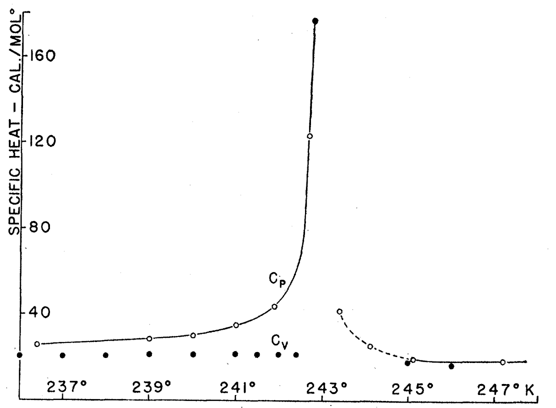

FIG. 9. The variation of c_p and c_v with temperature through the transition in polycrystalline ammonium chloride. The circles represent the data of Simon, von Simson and Ruheman.

Frenkel,[28] on the other hand, argues against the inception of free rotation at the transition on the ground that there is no supporting evidence for the implied concurrent weakening of the interatomic binding force. Frenkel's view is that the tetrahedra execute rotational *oscillations* both below and above the transition temperature; that below it there exists an order in the orientations of the axes about which the oscillations occur; that at the transition temperature this order is destroyed, so that above it the

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[24] These results were reported at the Boston meeting of the American Chemical Society, in September 1939.

[25] R. H. Fowler, Proc. Roy. Soc. **A149**, 1 (1935); T. S. Chang, Proc. Camb. Phil. Soc. **33**, 524 (1937).

[26] The energy associated with the internal degrees of freedom of the ammonium ion is inappreciable at the temperatures here contemplated.

[27] L. Pauling, Phys. Rev. **36**, 430 (1930).

[28] J. Frenkel, Acta Physicochemica **3**, 23 (1935).

orientations are irregularly distributed throughout the lattice and, furthermore, may change discontinuously from time to time. This model yields the correct contribution to c_v above the transition and, in virtue of the cooperative nature of the phenomenon, accounts qualitatively for the higher value of c_v, *viz.* 22 cal./mol-deg., below it.

In conclusion the writer desires to acknowledge his indebtedness to Professor Krefeld and Mr. Kenyon, of the Department of Civil Engineering at Columbia University, for their cooperation and assistance in preparing the specimens; to Mr. Richard Scheib, for his constant aid in the construction and manipulation of the apparatus; and to Dr. S. L. Quimby, who followed the progress of the research with helpful counsel and encouragement.

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Paramagnetic Relaxation Times for Titanium and Chrome Alum

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The relaxation times for spin-lattice coupling in titanium and chrome alum are computed on the basis of a specific model obtained by combining the thermodynamic theory of Casimir and du Pré with the writer's previous treatment of the normal modes of a cluster of the form $X\cdot 6H_2O$, where X contains an incomplete shell. The calculation includes both the first-order or direct processes important at low temperatures, and the second-order or "Raman" type of term predominant in the liquid-air region. There is no difficulty in understanding the observed absence of dispersion in titanium alum at liquid-air temperatures, but, barring crystal imperfections, it is hard to understand this absence at helium temperatures unless the nearest excited states are unreasonably deep. The agreement between the orders of magnitude of the calculated and experimental relaxation times is adequate in chromium both at high and low temperatures. The calculations predict, in agreement with experiments, that at liquid-air temperatures the relaxation time should increase when a constant field H_0 is applied and should be independent of the direction of H_0. The computed increase, however, is apparently not great enough. At helium temperatures, τ is theoretically not quite isotropic, and $d\tau/dH_0$ has the wrong sign, unless one abandons the usual formula $\rho_\omega \sim \omega^2$ for the density of lattice oscillators. The calculations on chromium should also apply qualitatively to iron alum, discussed at the very end.

I. Introduction

A NOTEWORTHY series of experiments on magnetic absorption and dispersion in paramagnetic media at radio and lower frequencies have been performed within the last few years by Gorter and other Dutch physicists.[1] In solid bodies the spin and orbit are largely decoupled, and the magnetism results almost entirely from spin. At first sight, it may seem that, owing to this decoupling, the spin moment is a constant of the motion, and so does not undergo any of the oscillations prerequisite to absorption or dispersion. The constancy is, however, spoiled by "spin-spin coupling," i.e., interaction between the spins of different paramagnetic atoms, and also by a slight potential energy of alignment of spin relative to the crystal lattice which arises because the spin is never perfectly decoupled from the orbit, and so indirectly feels the influence of the crystalline Stark effect acting on the orbit. The measurements on absorption and dispersion are particularly instructive because of the light which they shed on (*a*) the relaxation time τ_s involved in spin-spin interaction and (*b*) that τ characteristic of the coupling between spin and lattice. The present paper is devoted to τ rather than τ_s. Ordinarily τ_s is small compared to τ and is unimportant at the frequencies employed experimentally. The most elegant way of determining τ is furnished by the thermodynamic treatment of Casimir and du Pré,[2]

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[1] See *Physica*, from 1936 on, or the dissertations of Brons and of Teunissen (Groningen, 1939).

[2] H. B. G. Casimir and F. K. du Pré, Physica **5**, 507; also especially Casimir, Physica **6**, 156 (1939).