PHYSICAL REVIEW B VOLUME 4, NUMBER 3 1 AUGUST 1971

Order-Disorder Transition in NH_4Cl. I. Phenomenological Theory*

Charles P. Slichter, Horst Seidel,[†] Paul Schwartz,[‡] and George Fredericks[§]
Department of Physics and Materials Research Laboratory,
University of Illinois, Urbana, Illinois 61801
(Received 3 August 1970)

A phenomenological theory is presented to explain the thermodynamic behavior of ammonium chloride near the first-order phase transition at 242 °K. The theory is similar to that of Garland and Renard for NH_4Cl and other theories for magnetic systems, but is cast in a form convenient for analysis of experimental data according to various scaling laws. The lattice system gives rise to nonsingular terms in the Helmholtz free energy of the total system. The order-disorder system gives rise to a singular term in the free energy. The coupling of the two subsystems then produces the possibility of the first-order transition.

I. INTRODUCTION

Ammonium chloride (NH_4Cl) is a solid with a CsCl-type crystal structure below 456 °K.[1] Two unit cells of the crystal are shown in Fig. 1. The nitrogen atoms in the ammonium ions sit at the body centers of the chlorine simple cubic lattice, and the N-H bonds point at the chlorine ions along the $\langle 111 \rangle$ axes of the lattice. The two possible orientations of the tetrahedral ammonium ion are shown in Fig. 1, where they are labeled a and b.

At a temperature near 242 °K, ammonium chloride undergoes a phase change which was first discovered by Simon,[2] who saw an anomalous peak in the heat capacity near 242 °K. The transformation is associated with the orientation of the ammonium ions. In the high-temperature state the probability of an ion being in orientation a is equal to the probability of it being in b. In the low-temperature state there is a preference for neighbors to be in the same orientation, and there is a macroscopic ordering of the ammonium ions.[3]

Because of the basic two-state nature of the problem, it is natural to try to associate the behavior of ammonium chloride near this transition with the properties of the Ising model. The two orientations of the ammonium ions can be associated with the two states of the Ising spin. Such an identification leads one to expect a second-order transition. However, careful experimental studies reveal that ammonium chloride exhibits a volume discontinuity, and that it has hysteresis, i.e., the temperature of the transition depends upon whether one passes through it by heating or by cooling. The conversion of the transition from the expected second order to first order is due to the nonzero compressibility of the lattice. There is a good deal of work that shows how this transformation from second- to first-order behavior comes about.[4–9] Using a model in which the tetrahedral coupling is that of a two-dimensional Ising lattice and in which the lattice is considered compressible, Garland and Renard[10] have explained the main qualitative features of the transition.

In recent years, there have been a number of experimental and theoretical studies of second-order phase transitions near the transition temperature. It is our objective to compare the type of behavior predicted by various theories with experiment. To do so, we have developed an approach which incorporates the physical concepts of Garland and Renard but is convenient for comparing arbitrary critical behavior. In this paper we present the theory, and in the following two papers (first and second following papers, this issue) we apply the concepts to the study of the heat capacity and the thermal expansion.

II. CRITICAL BEHAVIOR IN A COMPRESSIBLE SYSTEM

Consider a system that has a singularity in the free energy such that the system would exhibit a second-order phase transition as the temperature is varied at constant interparticle spacing. For a given spacing the transition will occur at a temperture T_c. Since the microscopic interactions that are responsible for the transition will, in general, depend on the relative spacings of the particles in the system, the temperature T_c will also depend on these spacings. In a cubic or isotropic medium this means that T_c will depend on the volume V, which is a macroscopic measure of the average interparticle spacing.

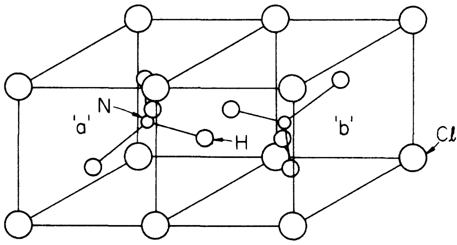

FIG. 1. Ammonium chloride structure.

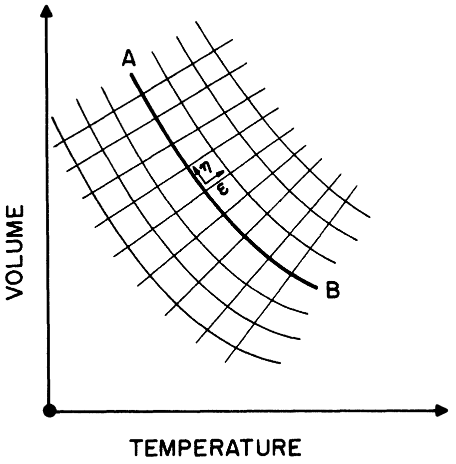

FIG. 2. Change of variables.

It has been argued by many workers in the field of phase transitions that the fluctuations in the system are of primary importance in determining the nature of the transition. Fisher[11] was the first to include the effects of volume fluctuations on the strength of the interactions and show that the transition could remain second order when observed at constant pressure. Baker and Essam,[12] Wagner,[13] and Wagner and Swift[14] have also shown that under various conditions this type of transition will remain second order, and thus they do not describe the volume discontinuity, latent heat, and temperature hysteresis which we observe experimentally for ammomium chloride. Therefore, in this paper we have chosen to neglect the effects of the fluctuations in interparticle spacing and include just the average effect of the volume on the interaction since the simple theory that results shows excellent qualitative agreement with the behavior of ammonium chloride. We will develop the theory in a quantitative manner which will permit us to examine the agreement between theory and experiment in the following two papers.

Within the context of the simple picture discussed above we look at the behavior of the Helmholtz free energy in the V-T plane. If we initially consider the system as a "rigid lattice," i.e., if we do not allow any variation in interaction potentials, the free energy will exhibit a singularity as a function of temperature that is characteristic of a second-order phase transition. We may consider a variety of such systems differing in their lattice constants. For them, the free energy A_s is a function of T and parametrically of V because of the volume dependence of the interaction strength. Thus, we can draw a line AB in the V-T plane along which A_s is singular (see Fig. 2). However, we may also consider A_s as a function of the orthogonal variables η and ϵ where lines of constant ϵ are parallel to AB, the singular line. A_s should be a well behaved function of η, and we should be able to make the following expansion which is valid everywhere except on the singular line:

$$A_s(\epsilon, \eta) = f_0(\epsilon) + \eta f_2(\epsilon) + \eta^2 f_3(\epsilon) + \cdots , \tag{1}$$

where the f_i is an unknown series of functions that may be singular on the line AB which is taken to be $\epsilon = 0$. If we now consider only a small volume of space about a point on the singular line, the singular line will be essentially straight. η and ϵ will be linearly related to T and V, and the coordinate transformation can be a simple rotation in the V-T plane.

So far we have described a *model*. In the case of ammonium chloride the phase transition is associated with the ordering of the ammonium tetrahedra. It is the interaction between the tetradehra that gives rise to the transition. In dealing with the *real system* one must recognize that the lattice is not rigid. There are three effects which result: (i) The average volume will be a function of the temperature; (ii) there will be fluctuations in the interparticle spacing around the average, i.e., there are more generalized coordinates needed to describe the atomic positions than just the average volume; (iii) the background lattice will contribute a nonsingular part to the free energy.

Our approximation consists of (a) neglecting the fluctuations in (ii) above, (b) considering A_s to be a function of two variables only—T and V or, equivalently, ϵ and η—(c) writing the total free energy as a sum of A_s and the nonsingular lattice contribution A_L,

$$A = A_L(V, T) + A_s(\epsilon, \eta) , \tag{2}$$

and (d) assuming various explicit forms for A_L and A_S, which will be discussed in what follows.

If we expand A_L about a point V_0, T_0 on the singular line we have

$$A_L(V, T) = A_0 - S_0(T - T_0) - p_0(V - V_0) - \frac{C_{V0}}{T_0}\frac{(T-T_0)^2}{2} + \frac{1}{\kappa_{T_0} V_0}\frac{(V-V_0)^2}{2} - \frac{\beta_0}{\kappa_{T_0}}(V - V_0)(T - T_0) , \tag{3}$$

where the symbols A_0, S_0, p_0, etc. may be viewed simply as coefficients in an expansion, but a notation has been used which suggests their conventional physical significance.

A possible form for A_s is

$$A_s = a_0 - a_\pm |\epsilon|^{2-\alpha_\pm} , \tag{4}$$

where $\epsilon = 0$ is the singular line and where a_+ and α_+ refer to points above the singular line in the disordered phase and a_- and α_- refer to points below the singular line in the ordered phase. a_0 is simply a constant. Henceforth the ± subscripts will be left off for simplicity. In the approximation that the singular line is straight, we have

$$\epsilon = \frac{T - T_0}{T_0} + n\,\frac{V - V_0}{V_0} = \frac{\Delta T}{T_0} + n\frac{\Delta V}{V_0}\ , \tag{5}$$

where the second equation defines ΔT and ΔV. The slope of the singular line is $-nT_0/V_0$, while T_0 and V_0 locate a point on the singular line about which the approximations are valid. For the special case of n equal to zero, ϵ takes the form $(T - T_0)/T_0$ and T_0 plays the role of a critical temperature in Eq. (4). Equation (4) corresponds to only taking the first term in the expression of Eq. (1).

Then using Eqs. (2)–(4) in the thermodynamic relation relating pressure to free energy

$$-p = \frac{\partial A}{\partial V}\bigg|_T\ , \tag{6}$$

we obtain the relation

$$-p = -D'a\frac{n}{V_0}(2-\alpha)|\epsilon|^{1-\alpha} - p_0 + \frac{1}{\kappa_{T_0}V_0}\,\Delta V - \frac{\beta_0}{\kappa_{T_0}}\,\Delta T\ , \tag{7}$$

where $D' = +1$ if $\epsilon > 0$ and $D' = -1$ if $\epsilon < 0$. This equation gives an implicit relation between V, T, p.

The thermal-expansion coefficient β at zero pressure can be obtained from Eq. (7) by setting $p = 0$ and taking the temperature derivative:

$$\beta V_0 = \frac{\beta_0 V_0 + (a\kappa_{T_0} n/V_0 T_0)(2-\alpha)(1-\alpha)|\epsilon|^{-\alpha}}{1 - a\kappa_{T_0} n^2(2-\alpha)(1-\alpha)|\epsilon|^{-\alpha}/V_0}\ . \tag{8}$$

Using the relation

$$C_p = -T\frac{\partial}{\partial T}\bigg|_p\left(\frac{\partial A}{\partial T}\right)_V \tag{9}$$

and Eqs. (2)–(4) we obtain

$$C_p = C_{V_0} + \frac{a(2-\alpha)(1-\alpha)}{T_0}\,|\epsilon|^{-\alpha} + \beta V_0[(\beta_0 T_0/\kappa_{T_0}) + an(2-\alpha)(1-\alpha)|\epsilon|^{-\alpha}]\ . \tag{10}$$

An example of a system that fits the above scheme is the Ising system on a compressible lattice. If we assume weak coupling between the Ising system and the lattice, the Hamiltonian for this system is

$$\mathcal{H} = \mathcal{H}_L + \mathcal{H}_I\ . \tag{11}$$

The usual nearest-neighbor rigid-lattice Ising model studied has the Hamiltonian

$$\mathcal{H}_{\mathrm{IRL}} = -J\sum_{i,j}\sigma_i\sigma_j\ . \tag{12}$$

The simplest way of taking the distance dependence of the interaction between the ammonium ions into account is to replace the constant J by a function of the volume. Then

$$\mathcal{H}_I = -J(V)\sum_{i,j}\sigma_i\sigma_j\ . \tag{13}$$

Applying statistical mechanics to this Hamiltonian, we find the Helmholtz free energy for the ammonium chloride system:

$$A = A_L(V, T) + A_I(J(V), T)\ . \tag{14}$$

Here $A_I(J, T)$ is the free energy of the system described by the Hamiltonian in Eq. (12), and A_L is the Helmholtz free energy of the background lattice.

By using elementary statistical mechanics, it can be shown that

$$A_1(J(V), kT) = -kT\Phi(J(V)/kT)\ , \tag{15}$$

where $\Phi(J(V)/kT)$ is the logarithm of the partition function. Since the background lattice has no phase transition, the free energy A_L will be a nonsingular function and may be expanded in a power series as in Eq. (3).

The physical properties of the total system can now be found using Eqs. (2), (3), (6), (9), and (5). We find

$$-p = -p_0 + \frac{1}{\kappa_{T_0}V_0}\,\Delta V - \frac{\beta_0}{\kappa_{T_0}}\,\Delta T - \Phi'J'\ , \tag{16}$$

$$-p = -p_0 + \frac{1}{\kappa_{T_0}V_0}\,\Delta V - \frac{\beta_0}{\kappa_{T_0}}\,\Delta T - \frac{J'}{J}\,U_I \tag{17}$$

and

$$C_p = C_{V_0} + C_I + \beta V_0\left\{\frac{\beta_0 T_0}{\kappa_{T_0}} + J'\left[\Phi' - \Phi''\left(1 + \frac{J}{kT}\right)\right]\right\}, \tag{18}$$

$$C_p = C_{V_0} + C_I + \beta V_0 T_0\left[\frac{\beta_0}{\kappa_{T_0}} - \frac{J'}{J}\left(C_I + \frac{U_I}{T_0}\right)\right]. \tag{19}$$

Here

$$A' = \frac{dA(x)}{dx}\ ,\quad J' = \frac{dJ(V)}{dV}\ ;$$

$$U_I = \frac{-\,\partial(A_I/kT)}{\partial(1/kT)}$$

is the internal energy of the Ising system; and $C_I = (J/kT)^2 K\Phi'' = -(U_I' J/kT^2 + 2U_I/T)$ is the constant-volume heat capacity of the Ising system.

Note that C_p contains β, the thermal expansion of the total system. It can be found by taking the derivative of Eq. (17) with respect to temperature at constant pressure:

$$\beta V_0 = \frac{\beta_0 V_0 - \kappa_{T_0} V_0 (J'/J) C_I}{1 - \kappa_{T_0} V_0[(J'/J)^2 T C_I - U_I (J'/J)]}\ . \tag{20}$$

Since J' should be negative for a system like ammonium chloride, and C_I should be positive, the numerator of β will always be positive. Also, in the neighborhood of the second-order phase transition U_I or Φ' should be much more slowly varying

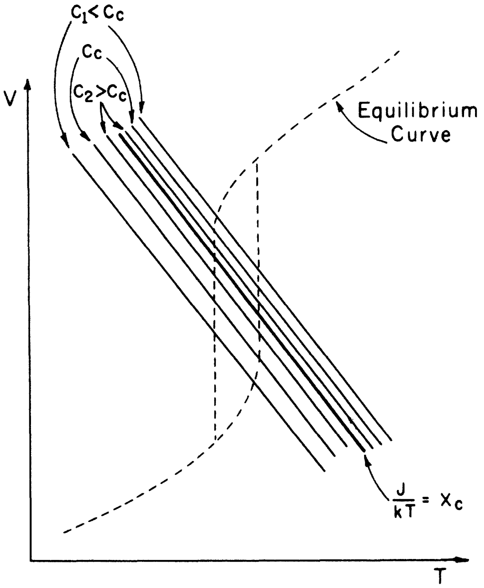

FIG. 3. Volume-temperature relation predicted by the theory when C_I exceed C_C near the singular line.

than C_I. Then, if the heat capacity of the Ising system reaches a critical value

$$C_C \cong \frac{1}{\kappa_{T_0} V_0 T}\left(\frac{J}{J'}\right)^2 , \tag{21}$$

β will go to infinity. In passing through the infinity β will change sign. Since β is the dominant term in C_p at this point, the heat capacity also changes sign. This sign change also occurs in κ_T, the isothermal compressibility. These sign changes in κ_T and C_p are forbidden thermodynamically and are an indication that the system undergoes a first-order phase change to maintain stability.

In Fig. 3 there is a schematic representation of the prediction of this model when C_1 exceeds C_C at the second-order transition. The critical line $J/kT = x_c$ represents the line of second-order transitions for the Ising system. Contours of constant C_I are drawn near it, and the dashed curve represents the V-T relation predicted by the model.

In order to go beyond the general equations found above, some form must be assumed for $J(V)$ and A_I.

For J, a reasonable form that has the proper sign for the first derivative is

$$J = J_0 V_0^n / V^n . \tag{22}$$

In the neighborhood of the expansion point this becomes

$$J \simeq J_0 (1 - n\,\Delta V/V_0) . \tag{23}$$

For A_I, it is desirable to choose a function that will easily relate to the theory. One possibility is to use the results of some calculation such as the exact solution of the two-dimensional Ising model as Garland and Renard did. Another such result is found in the work of Wakefield[15] on the Ising model in a simple cubic lattice.

A function which is commonly used to characterize the critical behavior of the heat capacity near a second-order phase transition is

$$C_I \sim |\epsilon|^{-\alpha} , \tag{24}$$

where $\epsilon = (T - T_c)/T_c$ and $J/kT_c = x_c$ is the singular point of the free energy. Then a good choice for A_I is

$$A_I = -a_\pm |\epsilon|^{2-\alpha\pm} + a_0 , \tag{25}$$

where

$$\epsilon = \Delta T/T_0 + n\,\Delta V/V_0 , \quad J_0/kT_0 = x_c . \tag{26}$$

This choice of ϵ puts the expansion point V_0, T_0 on the singular line of A_I and is obtained by expanding the relation $J(V)/kT = x_c$ to lowest order in ΔV and ΔT. Now contact is made between the compressible Ising system and the earlier general assumptions.

The parameter n expresses the strength of the volume dependence of the interaction responsible for the transition. For the ammonium chloride system the interaction is that between the ammonia tetrahedra. Part of the interaction is Coulombic and may be expressed as the sum of interactions of the electrostatic multipoles of the tetrahedra. The lowest-order nonzero term that depends on the relative orientation of the tetrahedra is the octupole-octupole interaction.

The other part of the interaction is classified non-Coulombic[16] and may come from a hard-core potential that exists between the ions or perhaps from hydrogen-bonding effects.[16] There is not sufficient information about the volume dependence of the parameters involved to obtain a theoretical value for n.

The other parameters appearing in the theory are harder to obtain theoretically. Much work has been done on the problem of second-order phase transitions, so in some cases the parameters in A_I may have been calculated. The properties of the lattice are even harder to calculate from first principles. Thus, the lattice parameters, as well as any of the parameters describing the Ising system, may be treated as adjustable numbers when comparing the predictions of the theory to the results of an experiment.

---

*Research supported in part by the U. S. AEC under Contract No. AT(11-1)-1198.

†Present address: Physikalisches Institut, Universität Stuttgart, Azenberg, Germany.

‡Present address: David Sarnoff Research Laboratory, Princeton, N. J. 08540.

[§] Present address: Department of Physics, University of Texas at Austin, Austin, Tex. 78712.

[1] J. Itoh and Y. Yamagata, J. Phys. Soc. Japan 17, 481 (1962).

[2] F. Simon, Ann. Physik 68, 241 (1922).

[3] H. A. Levy and S. W. Peterson, Phys. Rev. 86, 766 (1952).

[4] J. S. Smart, Phys. Rev. 90, 55 (1953).

[5] O. K. Rice, J. Chem. Phys. 22, 1535 (1954).

[6] C. Domb, J. Chem. Phys. 25, 783 (1956).

[7] C. P. Bean and D. S. Rodbell, Phys. Rev. 126, 104 (1962).

[8] P. C. Mattis and T. D. Schultz, Phys. Rev. 129, 175 (1963).

[9] R. A. Farrel and P. H. E. Meijer, Physica 31, 725 (1965).

[10] C. W. Garland and R. Renard, J. Chem. Phys. 44, 1120 (1966).

[11] M. E. Fisher, Phys. Rev. 176, 257 (1968).

[12] G. A. Baker, Jr. and J. W. Essam, Phys. Rev. Letters 24, 447 (1970).

[13] H. Wagner, Phys. Rev. Letters 25, 31 (1970).

[14] H. Wagner and J. Swift, Z. Physik 239, 182 (1970).

[15] A. J. Wakefield, Proc. Cambridge Phil. Soc. 47, 799 (1951).

[16] C. W. Garland and J. S. Jones, J. Chem. Phys. 41, 1165 (1964).

PHYSICAL REVIEW B VOLUME 4, NUMBER 3 1 AUGUST 1971

Order-Disorder Transition in NH_4Cl. II. Thermal Expansion*

George E. Fredericks[†]
Department of Physics and Materials Research Laboratory,
University of Illinois, Urbana, Illinois 61801

(Received 3 August 1970)

The thermal expansion of ammonium chloride has been measured in the neighborhood of the order-disorder transition near 242 °K. At 1 atm, the transition is found to be first order with a hysteresis of 0.21 °K. The measured thermal expansion shows sample dependence. The volume-versus-temperature data are fitted using the theory presented in the first paper of this series. These fits show qualitative agreement between theory and experiment, but systematic deviations outside the experimental scatter are found, especially near the transition. Values of the critical exponents α_+ and α_- of 0.97 and 0.75, respectively, were found to give the best fit to the data, in striking disagreement with theoretical calculations using the Ising Model.

I. INTRODUCTION

The suggestion that the phase transition of an Ising system on a compressible lattice might become first order has been made by a number of workers.[1-6] Ammonium chloride has been extensively studied in this regard.[7] Since the work reported here was completed, there has been further theoretical work on the compressible Ising system by Baker and Essam,[8] Wagner,[9] and Wagner and Swift.[10] In this later work it is shown that if the lattice spacing is allowed to accommodate locally to the spin fluctuations then the first-order transition of the earlier theory goes away.

However, at 1 atm, the transition in ammonium chloride is first order experimentally. Consequently, a test of these earlier theories for ammonium chloride is still worthwhile. It is quite possible that the results of these earlier theories will find better theoretical justification as time goes on.

One of the most straightforward tests of the theory of the first paper in this series is to see whether or not it can account for the volume-versus-temperature data for ammonium chloride. The thermal expansion of ammonium chloride has been measured by a number of workers. A list of references to their work has been compiled by Sakamoto.[11] Boiko[12] has also made a recent measurement of the thermal expansion by x-ray diffraction. We undertook to remeasure the thermal expansion to a higher resolution in order to make a better test of the theory of the transition.

II. EXPERIMENTAL TECHNIQUE

The temperature of the sample chamber was stabilized by the following method. The chamber was a 1-kg cylinder of copper. This cylinder was suspended in vacuum by two ½-in.-diam 0.010-in.-walled stainless-steel tubes. The sample chamber was surrounded by an annular tank filled with liquid nitrogen. A copper flange about 15 cm above the sample chamber provided thermal contact between the nitrogen tank and the stainless-steel tubes. The sample chamber was wound with 70 Ω of nichrome heater wire. Temperature control then involved supplying the correct power to the heater to balance the heat flow to the nitrogen tank.

A thermistor was glued directly to the heater with thermally conducting epoxy. This thermistor was placed in one arm of a Wheatstone bridge, whose voltage source was the reference output of a PAR JB-5 lock-in amplifier. The off-balance signal of the bridge went to a PAR CR-4 low-noise pream-