THERMODYNAMIC PROPERTIES OF AMMONIUM HALOGENIDES NEAR THEIR TRICRITICAL POINTS

E. B. Amitin, Yu. A. Kovalevskaya,
I. E. Paukov, and K. S. Sukhovei

UDC 536.63

A study was made pertaining to anomalies of the specific heat of NH_4Cl and of $NH_4Cl_{1-x}Br_x$ solid solutions. It has been discovered that in addition to a classical tricritical behavior ($\alpha = 0.5$) there can also occur "Ising" anomalies (α 0.1) in the vicinity of tricritical points.

The behavior of an ideal system in the vicinity of its phase transition point T_c of the second kind is quite adequately described on the basis of prevailing theoretical concepts. It is well known the anomalies of the thermodynamic functions near these points can be characterized by power-law relations for the referred temperature $\tau = (T - T_c)/T_c$. The value of the critical power exponent can be determined approximately by the renorm-group method and they agree closely enough with experimental data in the case of simple nearly ideal systems. In real solids the hardening process is often complicated by various secondary effects, which can completely alter the anomalies of thermodynamic properties in the vicinity of the disordering point. One of the most interesting anomalies in the behavior of such complex real systems is the instability effect and jumpwise disordering. In such substances there occurs a phase transition of the first kind which is near that of the second kind. Phase transformation begins far from the critical point, just as one of the second kind, but at some temperature the system becomes unstable and at this point transition is completed by a jumpwise change in the order parameter and of other thermodynamic parameters, which is characteristic of phase transition of the first kind. As the external parameters of such a system (pressure, concentration, fields) are varied, there can occur a change from one kind of behavior to the other, i.e., from transition of the first kind to transition of the second kind or vice versa. The system has then a so-called tricritical point. On the phase diagram this is a singular point, where the line of transitions of the first kind without discontinuity becomes a line of transitions of the second kind.

For a study of triple-point phenomena, we had selected the NH_4Cl—NH_4Br system. The ordered elements in this system are NH_4 tetrahedra, which can have two different orientations in the cubic lattice of the halogens. In this respect, the system is analogous to the Ising model. Accordingly, NH_4 tetrahedra can form two kinds of ordered structures: the δ phase corresponds to the ferromagnetic kind of ordering and the γ phase corresponds to the antiferromagnetic kind of ordering. The ordering process in NH_4Cl under atmospheric pressure proceeds as a phase transition of the first kind close to one of the second kind. Under pressures above 1.5 kbar it becomes a phase transition of the second kind. A change of the kind of phase transition is also expected in NH_4Cl—NH_4Br solid solutions.

The occurrence of phase transitions of the first kind close to those of the second kind in the NH_4Cl—NH_4Br system was originally attributed [1] to appreciable strictive-fluctuational interaction (compressible Ising lattice). Indeed, the parameter dT_c/dP characterizing the compressibility of a lattice has a value one order of magnitude higher for this system than for most magnetic systems. Lately, however, researchers are more inclined to regard competing interactions [2] as the decisive factor which brings about phase transitions of the first kind in this system. It is well known [3] that direct octupole—octupole interactions of tetrahedra can result in forming the δ phase only. The existence of a γ-phase structure can be explained by indirect interaction of tetrahedra through halogen ions [2]. The relative strengths of these interactions can be varied through external factors. Compression of the system will increases the role of direct octupole—octupole interaction.

Institute of Inorganic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 39, No. 6, pp. 1095-1099, December, 1980. Original article submitted July 3, 1979.

0022-0841/80/3906-1381$07.50

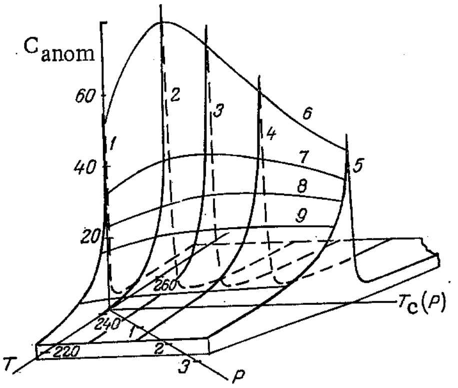

Fig. 1

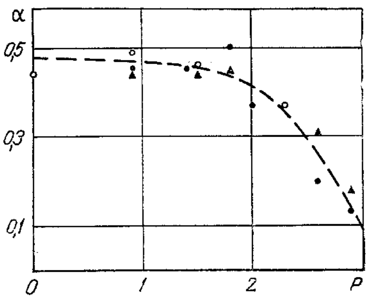

Fig. 2

Fig. 1. Surface of anomalous specific heat for NH_4Cl in the vicinity of the triple point: curves 1-5 pass through experimental points corresponding to pressures: 1) $P = 0$; 2) $0.3 < P < 1.5$ kbar; 3) $0.7 < P < 2.2$ kbar; 4) $1.3 < P < 3.0$ kbar; 5) $2.4 < P < 4.2$ kbar; isolines 6-9 correspond to sections of the surface where $T_c(P) - T$ is constant and equal to: 0.2, 0.5, 1, and 2°K, respectively; C_{anom} is in cal/mole·deg.

Fig. 2. Dependence of the critical exponent α for NH_4Cl on the pressure at temperature $T < T_c(P)$. Notation corresponds to various methods of mathematical processing of experimental data for construction of the $C_{anom}(P, T)$ surface and its isobaric sections.

In $NH_4Cl_{1-x}Br_x$ solid solutions, on the other hand, an increase of the bromine concentration will shift the relative strengths of direct interaction and indirect interaction in the opposite direction, i.e., increase the role of indirect interaction. The object of this study was to examine the thermodynamic properties of the NH_4Cl—NH_4Br system in the vicinity of phase transitions over a wide range of relative strengths of these competing interactions. Accordingly, we studied the anomalies in the temperature dependence of the specific heat of NH_4Cl under high pressure (up to 4 kbar) and over the 200-320°K temperature range. In parallel were also studied the anomalies of the thermodynamic properties of $NH_4Cl_{1-x}Br_x$ solid solutions. The specific heat of ammonium chloride under high pressure was measured with an adiabatic vacuum calorimeter. An autonomous high-pressure cylinder [4] was used as the calorimeter vessel. Since measurements in an autonomous vessel are not made under a constant pressure, supplementary experiments and appropriate mathematical processing of data were needed for obtaining the specific heat C_p at constant pressure. With the thus obtained three-coordinate $C_{anom}(P, T)$ curves, on the basis of altogether approximately 500 points, and by the method of spline functions was then plotted, with the aid of a computer, the surface of anomalous specific heat in the vicinity of phase transition lines (Fig. 1). The values of C_{anom} in isobaric sections of this surface were approximated with power functions

$$C_{anom} = A + B\tau^{-\alpha}$$

according to the method of least squares.

According to published data [5], the δ phase of NH_4Cl has a tricritical point at $P \cong 1.5$ kbar and $T \cong 256$°K. According to theory, a classical tricritical point of a system occurs where the coefficient of the fourth-order invariant in the Landau—Ginzburg—Wilson Hamiltonian becomes zero. Noncorrelated (Gaussian) fluctuations are then playing the main role in the anomaly of the thermodynamic properties of the system. The critical exponent α is 0.5 near such a Gaussian tricritical point. The pressure dependence of the critical exponent α according to our experiment is shown in Fig. 2. It is evident here that under pressures up to 1.8 kbar, the system behaves according to the classical description of a tricritical point. With rising pressure and farther away from the tricritical point, however, the value of the exponent gradually approaches that which corresponds to a plain phase transition of the second kind in the three-dimensional Ising model ($\alpha \cong 0.12$).

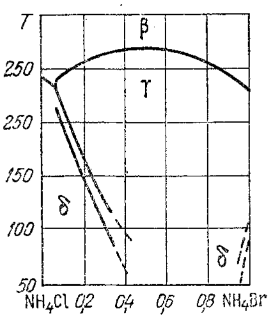

Fig. 3

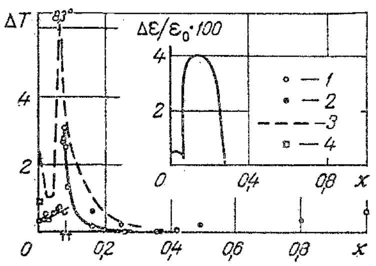

Fig. 4

Fig. 3. Phase diagram of the $NH_4Cl_{1-x}Br_x$ system.

Fig. 4. Hysteresis (ΔT°C) of the phase transition temperature as a function of the molar fraction x of bromine in the $NH_4Cl_{1-x}Br_x$ system: 1) data of study [6], 2) results of this study, 3) data of study [8], 4) data of study [9]; jump of the dielectric permittivity $\Delta\varepsilon/\varepsilon_0$ at the phase transition point as a function of the bromine concentration x, according to data in study [8].

The study continues with the anomalies of the thermodynamic properties of $NH_4Cl_{1-x}Br_x$ solid solutions in the vicinity of the tricritical point of its γ phase. The phase diagram of $NH_4Cl_{1-x}Br_x$ solid solutions is shown in Fig. 3. The process of disordering in the δ phase as well as in the γ phase near the tricritical point is a phase transition of the first kind with pronounced hysteresis effects and with jumpwise changes in volume and in the dielectric permittivity. At bromine concentrations higher than a 0.5 molar fraction there also appears a hysteresis of the transition point. The fact that the transition becomes less of the first kind at medium bromine concentrations [6-8] indicates that within this range of concentrations ($x = 0.2-0.5$) there must exist a range of phase transitions of the second kind which is on both sides bounded by tricritical points (Fig. 4).

The specific heat of $NH_4Cl_{1-x}Br_x$ solid solutions with $x = 0.25$, 0.37, and 0.5 respectively was measured over the 200-300°K temperature range. The specimens had been prepared from aqueous solutions of ammonium chloride and bromide with homogenization inside a sealed vessel at $T = 180°C$ for 40-80 h. The final composition and homogeneity of these specimens was checked by chemical and spectral analysis. The results of x-ray examination suggest that these solid solutions can be regarded as ideal ones. The deviation of their lattice parameter from Vegard's law did not exceed 0.01%.

Measurements of the hysteresis of the phase transition temperature have revealed that within the given range of bromine concentration there probably exists a range of phase transitions of the second kind. At any rate, for the specimen with $x = 0.37$ it was not possible, with our experimental accuracy ($\Delta T < 0.01°K$), to detect any hysteresis of T_C. The specific heat was measured in an adiabatic vacuum microcalorimeter with a 0.3 cm^3 large volume [10]. The normal part of the specific heat was determined just as in the earlier studies [11, 12]. The values of exponent α obtained for three specimens were found to correspond to the $\alpha = 0.1$ exponent in the three-dimensional Ising model. It is hardly probable that a range of classical tricritical behavior exists between the given bromine concentrations. Estimates of the width of such a range, if it existed, were made on the basis of comparison with the known width of this range for NH_4Cl and they indicate that the range of bromine concentrations with a classical tricritical power exponent would have to be $\Delta x = 0.2$ then. It therefore could not be detected in our experiments with the given specimens. It remains for us to assume that in this case we have encountered an anomalous tricritical point, one at which the anomalies of the thermodynamic properties are due to a buildup of correlated fluctuations. This is why our experiment has yielded the usual "Ising" value of exponent α in the vicinity of such a non-Gaussian tricritical point.

The possibility of existence of non-Gaussian tricritical points was predicted earlier in theoretical studies [13, 14] for special cases of a compressible system. Those studies have not answered the basic questions as to whether, e.g., there is a single criterion for the occurrence of such tricritical points and the behavior of systems in the vicinity of such points can be described unambiguously. We expect our results to attract the attention of researchers to many unanswered questions pertaining to nonclassical tricritical points.

NOTATION

α, critical power exponent of specific heat; C_{anom}, anomalous part of specific heat; C_p, specific heat at constant pressure; T_c, phase transition temperature; τ, referred temperature; P, pressure; and x, bromine concentration, in molar fractions.

LITERATURE CITED

1. C. W. Garland and R. Renard, "Order—disorder phenomena. Part 1: Instability and hysteresis in an Ising model near its critical point," J. Chem. Phys., 44, No. 3, 1120-1124 (1966).
2. V. G. Vaks and V. E. Shneider, "Theory of phase transition in ammonium halogenides," Preprint Inst. Fiz. SO-325, Krasnoyarsk (1975).
3. T. Nagamiya, "Theory of transformations in solid ammonium halogenides at low temperatures. Part 1: Ammonium chloride," Proc. Phys. Math. Soc. Jpn., 24, 137-164 (1942).
4. E. B. Amitin, Yu. A. Kovalevskaya, E. G. Lebedeva, and I. E. Paukov, "Measurement of heat capacity under high pressure: molar heat capacity of ammonium chloride near the order—disorder transition," High Temp.—High Press., 7, 269-277 (1975).
5. C. W. Garland and B. B. Weiner, "Changes in the thermodynamic character of the NH_4Cl order—disorder transition at high pressures," Phys. Rev. B, 3, No. 5, 1634-1637 (1971).
6. R. Jahn and E. Neumann, "Phase diagram of the solid-solution system $NH_4Cl_{1-x}Br_x$ as determined by optical methods," Solid-State Commun., 12, No. 7, 721-726 (1973).
7. C. J. Mandleberg and L. A. K. Staveley, "Phase transition studies in mixed crystals. Part 1: the NH_4Cl—NH_4Br system," J. Chem. Soc., 111-2, 2736-2743 (1950).
8. T. Gotô and Kan-Ichi-Kamiyosi, "Phase transition of $NH_4Cl_{1-x}Br_x$ mixed crystals," J. Phys. Soc. Jpn., 42, No. 6, 1924-1930 (1977).
9. C. W. Garland and C. F. Yarnell, "Temperature and pressure dependence of the elastic constants of ammonium bromide," J. Chem. Phys., 44, No. 3, 1112-1120 (1966).
10. K. S. Sukhovei, V. F. Anishin, and I. E. Paukov, "An adiabatic vacuum microcalorimeter with a 0.3-cm^3 volume for thermodynamic studies of substances within the 12-300°K temperature range," Zh. Fiz. Khim., 48, No. 6, 1589-1593 (1974).
11. M. Sorai, H. Suga, and S. Seki, "Phase transition in the ammonium bromide crystal: thermal motion of the ammonium ion," Bull. Chem. Soc. Jpn., 38, No. 7, 1125-1136 (1965).
12. E. B. Amitin, Yu. A. Kovalevskaya, É. G. Lebedeva, and I. E. Paukov, "Anomalies of the specific heat of ammonium chloride in the vicinity of the disordering point," Fiz. Tverd. Tela, 17, No. 9, 2549-2555 (1975).
13. A. M. Korotkikh and V. M. Nabutovskii, "Critical point of phase transitions of the first kind close to those of the second kind," Pis'ma Zh. Eksp. Teor. Fiz., 13, 208-211 (1971).
14. O. Entin-Wohlman, D. J. Bergman, and Y. Imry, "Tricritical phenomena in constrained systems," J. Phys. C: Solid-State Phys., 7, No. 3, 496-505 (1974).