On the Orientational Order-Disorder Transition in Crystalline Aniline Hydrobromide

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(Received August 1, 1960)

In the course of X-ray structural analyses⁽¹⁾ of aniline hydrobromide, Taguchi⁽²⁾ has recently observed a phase transition from the orthorhombic to the monoclinic system, which occurs on cooling at about 27°C. He also found that the monoclinic angle β, between the a and c axes, is not constant below the critical temperature but varies continuously over a wide range of temperature as the temperature is lowered. The detailed analyses of crystal structures above and below the transition temperature range were carried out by the same author. He found further anomalous spectra in oscillation and Weissenberg photographs below the critical temperature associated with the appearance of a hybrid structure. The detailed knowledge concerning the crystal structures above and below the transition temperature range, the unusual variation of the monoclinic angle, and the appearance of a hybrid structure stimulated us to study the thermal properties of this compound to look into the mechanism of this peculiar phase transition.

Experimental

Material. — Aniline (extra pure grade manufactured by Wakō Chem. Ind., Ltd.) was added to an excess of an aqueous solution of hydrobromic acid (1st grade, the same company). The precipitated salt was washed with cold distilled water and then recrystallized from warm ethanol. The crude product thus obtained was slightly colored and found to have some lattice imperfection as revealed by X-ray photographs⁽¹⁾. In order to purify the product further, it was finally subjected to fractional sublimation under high vacuum (10^{-5} mmHg). The final product obtained by this procedure is colorless powder. Single crystals were also obtained by sublimation. They are transparent and colorless

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1) I. Nitta, T. Watanabé and I. Taguchi, *X-rays*, 5, 31 (1948); to be published in this Bulletin.

2) I. Taguchi, This Bulletin **34**, 392 ((1961).

and are found to be free from lattice imperfection; m. p. 283°C.

Apparatus and Procedure.—For the preliminary study to ascertain the occurrence of the phase transition, a differential thermal analysis was carried out in the temperature range from −150 to +300°C. The apparatus was the same in its main feature as the one used hitherto in this laboratory[3] except for attachment of an automatic recording of the temperature difference between the sample and the reference substance (in this case, KCl). The detailed description of the recorder was recently given[4]. To determine the accurate transition temperature and to study the thermal behavior more in detail, measurements of heat capacity were also carried out in the temperature range from −80 to +60°C by the use of the conduction calorimeter[5]. For the heat capacity measurements 4.4 g. of the material was used, the heating rate being 0.25∼0.30°C/min. over the full temperature range. Further, the relative thermal expansion below and above the transition temperature as well as the hysteresis phenomenon associated with the phase transition were studied by employing a simple double-walled glass-made dilatometer filled with mercury as the confining liquid. About 29 g. of the material was used, and the heating and cooling rates were about 0.2°C/min.

Results

One of the typical curves of the differential thermal analysis is reproduced in Fig. 1. From this curve it was found that there is a comparatively broad thermal anomaly over the temperature range from −50 to +25°C, with sufficient reproducibility in the repeated measurements and also there is no detectable hysteresis either in the heating or in the cooling direction. The data of heat capacity in this temperature range are given in Table I and they are plotted in Fig. 2. As this figure shows, the excess heat capacity starts to rise gradually at about −70°C, reaches a maximum value at 22°C (critical temperature), and then drops down abruptly by as much as 9 cal./mol. deg. The general trend of the heat capacity versus temperature curve reminds us of the similarity to that of the order-disorder phase transition of binary alloy systems[6]. Table II gives enthalpy and entropy of the

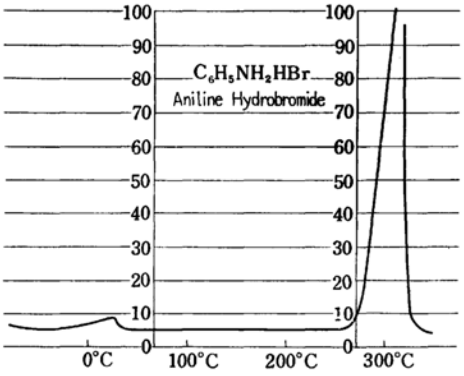

Fig. 1. Automatic recording curve of the differential thermal analysis for aniline hydrobromide.

TABLE I. HEAT CAPACITY DATA OF ANILINE HYDROBROMIDE

t°C	C_p(cal./mol. deg.)	t°C	C_p(cal./mol. deg.)
−73.93	28.62	2.63	40.64
−71.27	28.84	5.27	41.10
−68.08	29.24	7.88	41.80
−66.78	29.51	10.46	42.52
−63.28	29.93	13.01	43.16
−58.60	30.31	15.57	43.98
−53.91	30.98	18.10	44.69
−50.90	31.42	20.62	45.72
−47.83	31.81	23.18	42.60
−44.85	32.04	24.43	38.54
−41.85	32.41	25.60	38.13
−38.92	32.91	28.22	38.13
−36.01	33.34	31.98	38.26
−33.10	33.92	34.43	38.39
−30.23	34.39	38.12	38.60
−27.35	35.00	41.80	39.18
−24.58	35.56	44.21	39.31
−18.98	36.62	47.80	39.74
−16.21	36.99	50.22	40.22
−13.43	37.34	52.63	40.29
−10.73	38.11	55.03	40.64
− 8.04	38.54	61.00	41.63
− 5.35	39.11	64.53	42.00
− 2.67	39.71	66.88	41.81

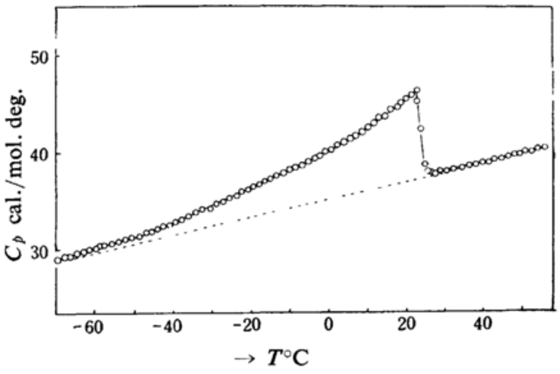

Fig. 2. Heat capacity versus temperature curve of aniline hydrobromide.

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[3] H. Chihara and S. Seki, ibid. **26**, 88 (1953); I. Nitta, S. Seki and H. Chihara, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **70**, 387 (1949).

[4] H. Suga, H. Chihara and S. Seki, ibid., **82**, 24 (1961).

[5] I. Nitta, S. Seki and M. Momotani, *Proc. Japan Acad.*, **26-9**, 25 (1950); S. Seki, M. Momotani, K. Nakatsu and T. Ōshima, This Bulletin, **28**, 411 (1955).

[6] H. Moser, *Physik. Z.*, **37**, 737 (1936); F. W. Jones and C. Sykes, *Proc. Roy. Soc.*, **A167**, 440 (1937).

TABLE II. HEAT AND ENTROPY OF TRANSITION AND DIFFERENCE OF HEAT CAPACITIES AT T_c

ΔH (transition)	297 ± 10 cal./mol.
ΔS (transition)	1.10 ± 0.05 e. u.
ΔC_p (at T_c)	~ 9 cal./mol. deg.

transition and the difference of heat capacities at the critical temperature. To evaluate the enthalpy of transition, the excess heat capacities over the dotted line given in the figure are integrated graphically. Here the dotted line is drawn as the normal contribution of the lattice vibration to the heat capacity. By dividing the abnormal part into many sections of temperature intervals, the entropy of transition was evaluated by summing up the quotients obtained by dividing each area of these sections with the corresponding mean absolute temperature. The entropy of transition thus obtained, 1.10 e. u. is comparable in magnitude with those of NH$_4$Cl and ND$_4$Cl7) at their lambda point, 1.30$\sim$1.40 e. u. As is evident from Fig. 2, the heat capacity curve is of typical lambda type and there is no indication of the latent heat at the critical temperature, showing that this transition is of higher order nature.

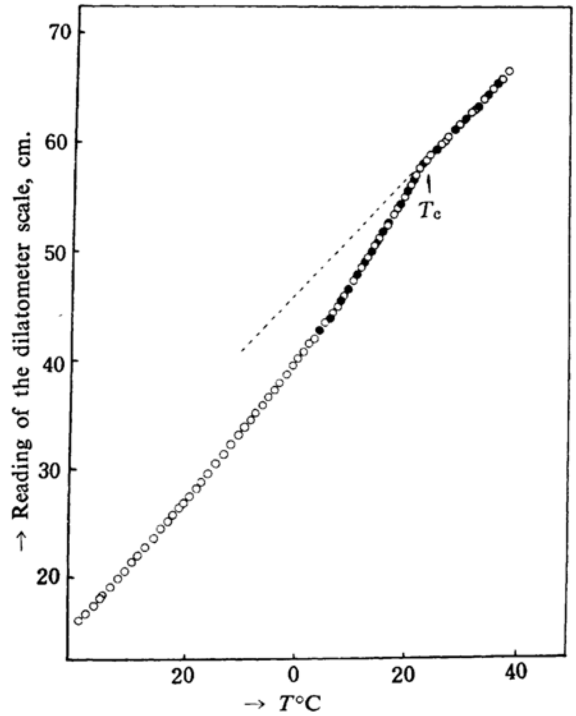

Fig 3. Volume versus temperature curve of aniline hydrobromide.

○ heating direction ● cooling direction

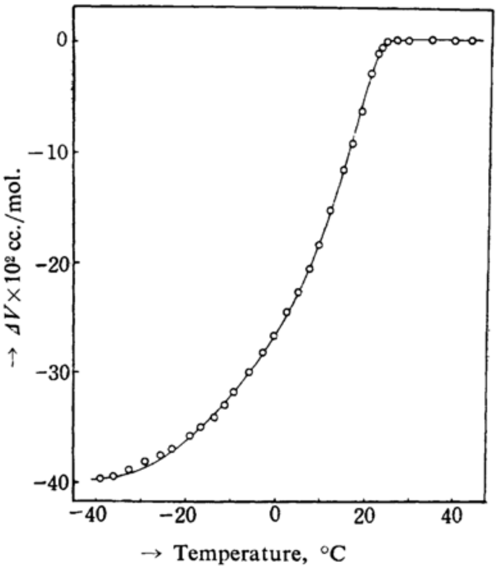

Fig. 3a. Anomalous thermal contraction of aniline hydrobromide.

Dilatometric studies revealed also the existence of abnormal expansion over the same transition range, as shown in Fig. 3. In this figure one can see that all the observed points in the heating and cooling directions can be represented by one and the same curve, showing again no hysteresis phenomenon. The dotted line in this figure means the thermal contraction extrapolated from the curve above the critical temperature by the use of the method of least squares. Fig. 3a gives the excess contraction ΔV below the dotted line and Fig. 4 the "abnormal" expansion coefficient calculated by $(1/V_0)\mathrm{d}(\Delta V)/\mathrm{d}T$, where V_0 is the molar volume of the crystal at the critical temperature. Although the expansion coefficient changes discontinuously at the critical point, the volume itself changes continuously over the whole range of measurements. These facts

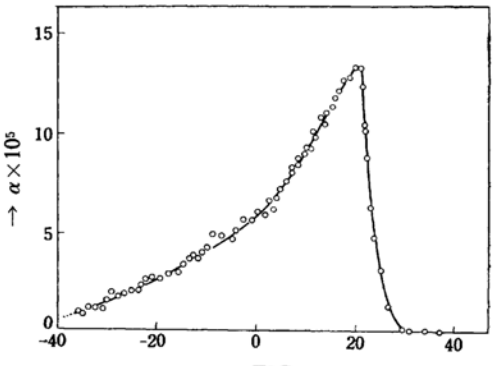

Fig. 4. Abnormal expansion coefficient of aniline hydrobromide.

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7) C. C. Stephenson, R. W. Blue and J. W. Stout, *J. Chem. Phys.*, 20, 1046 (1952).

also reasonably support the proposition that the transition is of higher order nature. The fact of non-existence of hysteresis phenomenon in the higher order phase transition was interpreted by Staveley et al.[8] from the point of view of lattice strain energy accompanying the phase transition.

Discussion

Prior to the discussion of the plausible mechanism of this phase transition, it is necessary to give a brief account of the crystal structure[1,2] above and below the critical temperature. The high temperature phase belongs to the orthorhombic system ($D_{2h}^{10}-Pnaa$). In this structure, it is required from the crystal symmetry that both the principal axis of anilinium ion ($N-C_1\cdots C_4$ axis) and the Br^- ion are found to lie on two different two-fold symmetry axes along the a axis. Although the positions of hydrogen atoms attached to the nitrogen atom are not yet determined, $-NH_3^+$ ionic group is surrounded by four Br^- ions, of which two are slightly more distant than the other two. On cooling the crystal through the critical temperature, it is transformed into the monoclinic system ($C_{2h}^5-P2_1/a$); the monoclinic angle deviates gradually from 90° and reaches 91°22′ asymptotically in a manner shown in Fig. 8, where the unit of the ordinate is twice the quantity $\Delta\beta(=\beta-90°)$, for convenience. In the structure of the low temperature modification, the requirement of two-fold symmetry imposed to the C–N axis is lost. In this phase, in response to the variation of β, the positions of Br^- ions and $-NH_3^+$ ionic groups are displaced with respect to each other, with the following sequence that the interionic distances between Br^- ions and an $-NH_3^+$ ionic group become different from each other, and also that the pseudo electric dipole moments due to the displacements of the two kinds of ions in the neighboring ionic array along the a axis may be found to be anti-parallel with each other in a similar manner as in the anti-ferroelectric crystal which was proposed originally by Kittel[9].

Considering the crystal structures as well as the thermal behaviors above and below the critical temperature described above it is suggested that a mechanism of orientational order-disorder of the $-NH_3^+$ group as an interpretation of this phase transition be given, based on the reason given below. In the first place, it will be natural to assume the pyramidal configuration (C_{3v}) of the $-NH_3^+$ ionic group. In the high temperature phase, since the C–N axis should lie on the two-fold symmetry axis, the potential energy of $-NH_3^+$ group associated with the rotational motion of this group will also have the same two-fold axial symmetry around this axis. Therefore, one has to consider necessarily some statistical randomness for the azimuthal orientation of $-NH_3^+$ group with respect to the C–N bond so far as one puts an $-NH_3^+$ group having three-fold symmetry on the axis of two-fold symmetry. On the other hand, in the low temperature phase such a requirement of two-fold symmetry is lost owing to the different crystal symmetry. Taking into account the possible formation of the $N-H\cdots Br$ weak hydrogen bond, possible orientations of the $-NH_3^+$ group with respect to the hydrogen atoms may be expected to be such as are represented in Fig. 5.

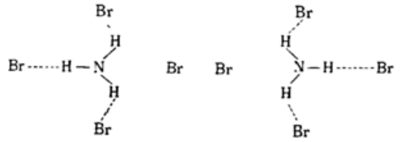

Fig. 5. Possible orientations of $-NH_3^+$ group (a- and b-types).

It is obvious from the symmetry consideration that these a- and b-type orientations are equally probable in the orthorhombic phase, whereas in the monoclinic phase one of these two types would be stabilized. We shall call this the a-type for convenience. Then, the requirement of two-fold axial symmetry in the high temperature phase will be satisfied if we distribute the $-NH_3^+$ groups between these two equilibrium orientations (a- and b-types), statistically in space and time. Thus, we may call tentatively this transition the "orientational order-disorder" type in the sense that an equal number of the a- and b-type orientations of $-NH_3^+$ groups can exist above the critical temperature whereas the number of the a-type orientation is predominant below the critical temperature. A simplified hindering potential energy curve for such a rotational motion of the $-NH_3^+$ group in the lattice may be represented schematically as in Fig. 6. This potential energy curve has 60° periodicity in the high temperature phase, while that corresponding to the low temperature phase will have 120° periodicity. As is shown in the figure, the degree of increase or decrease in depth of potential minima is assumed to be a linear function of $\Delta\beta$. Since the extent of displacement of the atomic position is assumed to be proportional to the variation of macroscopic quantity β in a first approximation, some of the physical properties of the present crystal

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[8] D. G. Thomas and L. A. K. Staveley, *J. Chem. Soc.*, **1951**, 2572.
[9] C. Kittel, *Phys. Rev.*, **82**, 729 (1951).

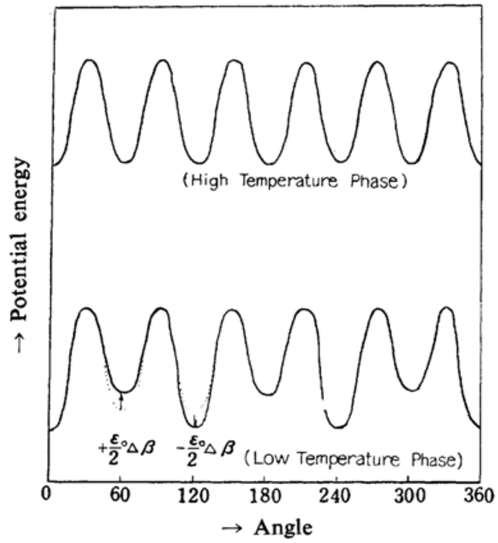

Fig. 6. Schematic representation of hindering potential for the rotational motion of $-NH_3^+$ group.

associated with the variation of β may be considered to change proportionally with the variation of β. As a matter of fact, Horie et al.[10] have recently given an example of the temperature dependence of the angle between optic elasticity axes, γ, in adjacent domains in the hybrid structure of aniline hydrobromide in the vicinity of the critical temperature (Fig. 7); one can see here a fairly linear relationship between the temperature variation of $\Delta\beta$ and γ.

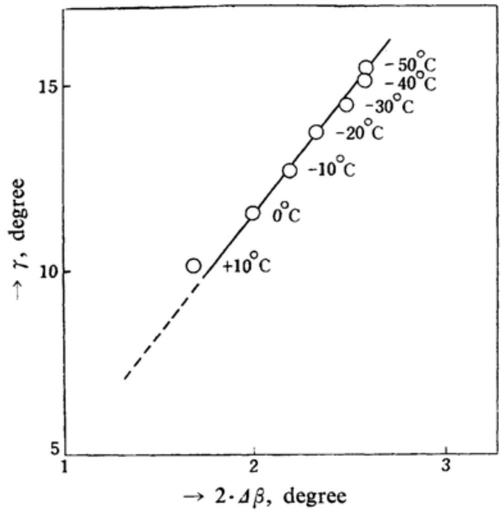

Fig. 7. Linear relationship between the temperature variation of $\Delta\beta$ and of the angle γ between the two optic elasticity axes in adjacent domains (after Horie et al.[10]).

Now, let us calculate the temperature dependence of $\Delta\beta$ on the basis of the proposed model in order to compare the result with the experimental value reported by the X-ray method[2]. We define the degree of order s as follows; let it be assumed that in a state specified by a set of values (T, s), $N(1+s)/2$ $-NH_3^+$ groups in the a-type orientation and $N(1-s)/2$ in the b-type are distributed over the whole N lattice points. The order parameter s thus defined has the same character as the one proposed for the theory of order-disorder phase transition of binary alloy[11]. That is, when $s=1$ all the $-NH_3^+$ groups are in the a-type orientation; this corresponds to the state of perfect order. When $s=0$ there are as many a-type groups as b-type groups; the state of complete disorder. It is somewhat difficult to calculate the hindering potential energy for rotational motion of the $-NH_3^+$ group in the crystalline field owing to an ambiguity in the estimation of effective charge distribution of the $-NH_3^+$ group, the unknown N-H distance and also the complexity of the crystal structure, so that we shall confine our calculation at the present stage only to the differences in the energy and entropy between the two phases. The notation Δ used in the following calculation stands for the excess of any thermodynamic quantities of the ordered state over that of the completely disordered state extrapolated above the transition point. The difference in the internal energy ΔU will consist of two parts in its origins; one is the contribution from the variation of the arrangements of ions and ionic groups and the other is that from the change of orientations of $-NH_3^+$ ionic groups when the ordered state changes to the disordered state. The first part of energy difference, ΔU_1, may be expressed formally by a power series in $\Delta\beta$ of which all the odd terms are omitted by the requirement that ΔU should be an even function of $\Delta\beta$, because the gradual change of either direction from the orthorhombic to the monoclinic crystal system should produce the same energy change. For example, the electro-static part of ΔU_1, which is the mutual interaction energy between the pseudo electric dipole moments produced by the displacements of ions and ionic groups, is expressed by

$$-1/2\sum_{i>j}\frac{\mu_i\mu_j}{r^3_{ij}}\{3\cos(\theta_i+\theta_j)+\cos(\theta_i-\theta_j)\}$$

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[10] T. Horie. T. Iwai and I. Taguchi, Annual Meeting of Phys. Soc. Japan, 1956,: To be published in near future. The author would like to express his appreciation for their permission to refer to their result before its publication.

[11] W. L. Bragg and E. L. Williams. *Proc. Roy. Soc.*, **A145**, 699 (1934); **A151**, 540 (1935); F. C. Nix and W. Shockley, *Rev. Mod. Phys.*, **10**, 1 (1938).

where μ_i, μ_j, θ_i, θ_j and r_{ij} have the usual meanings. Since μ_i and μ_j may be reasonably considered to be proportional to $\Delta\beta$, the term may be rewritten by $J(\Delta\beta)^2$, where J is a constant. If the higher terms in $\Delta\beta$ can be neglected, then $\Delta U_1 = A(\Delta\beta)^2$, where A is another constant. The second part of energy difference ΔU_2, which is due to the change of potential energy at an -NH$_3^+$ group caused by the variation of the degree of order s, may be expressed by $\frac{1+s}{2}N\left(-\frac{\varepsilon_0}{2}\Delta\beta\right)+\frac{1-s}{2}N\left(\frac{\varepsilon_0}{2}\Delta\beta\right)$ In this case it has been assumed that the change in the depth of potential minima is proportional to the change in $\Delta\beta$ with a constant of proportionality $\varepsilon_0/2$ (see Fig. 6). Thus,

$$\Delta U = \Delta U_1 + \Delta U_2 = A(\Delta\beta)^2 - sE\Delta\beta/2 \qquad (1)$$

where $E = N\varepsilon_0$.

On the other hand, the entropy difference ΔS is given approximately by the possible number of $N(1+s)/2$ a-type and $N(1-s)/2$ b-type arrangements of -NH$_3^+$ groups over the N whole lattice points.

$$\Delta S = \boldsymbol{k}\ln\frac{N!}{\left(\frac{1+s}{2}N\right)!\left(\frac{1-s}{2}N\right)!} - \boldsymbol{R}\ln 2$$

$$= -\boldsymbol{R}\left\{\frac{1+s}{2}\ln\frac{1+s}{2}+\frac{1-s}{2}\ln\frac{1-s}{2} + \ln 2\right\} \qquad (2)$$

Here, the additional term $\boldsymbol{R}\ln 2$ appears since the completely disordered state was taken as the reference. Accordingly, the difference of Helmholtz free energy ΔF between the two phases is given by

$$\Delta F = \Delta U - T\Delta S = A(\Delta\beta)^2 - sE\Delta\beta/2 + \boldsymbol{R}T\left\{\frac{1+s}{2}\ln\frac{1+s}{2}+\frac{1-s}{2}\ln\frac{1-s}{2} + \ln 2\right\} \qquad (3)$$

By the equilibrium conditions, we can obtain the following set of equations. From $\partial(\Delta F)/\partial(\Delta\beta)=0$ (since there is no external shear stress), it follows

$$\Delta\beta = Es/(4A) \qquad (4)$$

$$\Delta U = -E^2s^2/(16A) \qquad (4')$$

Eq. 4′ shows that the present treatment corresponds formally to the Bragg-Williams approximation. From $\partial(\Delta F)/\partial s=0$, we have

$$s = \tanh E^2 s/(8\boldsymbol{R}AT) \qquad (5)$$

$$T_c = E^2/(8\boldsymbol{R}A) \qquad (6)$$

where T_c is the critical temperature, above which s becomes zero. Inserting the value of s derived from 5 into 2, we get a calculated total entropy change 0.83 e. u. (−70∼+35°C) in comparison with the observed value 1.10 e. u. In this case, the additional entropy increment due to the increase of the available volume of ion, which may be reasonably given by $\boldsymbol{R}\ln(V+\Delta V)/V$, is quite negligible in magnitude, less than 0.01 e. u., in the same temperature interval. Combination of Eqs. 5 and 6 with Eq. 4 gives the temperature dependence of $\Delta\beta$ including the numerical factor $E/(4A)$, which can be determined, for example, by fitting the calculated value with the observed value of $\Delta\beta$ at a single temperature, say −40°C. The temperature dependence of $\Delta\beta$ obtained in this way is given by the dotted line in Fig. 8. Although qualitative agreement is obtained, the details are not fully explained especially in the following points; one is that the degree of covergence of this curve to the critical point is not so steep as that of the experimental curve, and another point is that the calculated $\Delta\beta$ should increase to 1.37 times as large a value as that at −40°C if the curve is extrapolated to 0°K, while the corresponding value obtained by experiment[2)] is only 1.12.

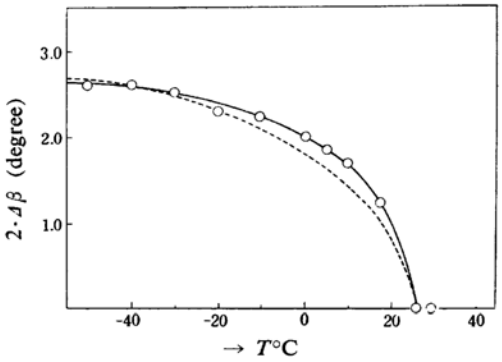

Fig. 8. Comparison of observed temperature variation of $\Delta\beta$ with the theoretical one.
○ Observed by Taguchi[2)]
---- Theoretical curve ignoring volume effect.
—— Theoretical curve including volume effect.

As already mentioned, an anomalous thermal expansion in the vicinity of the critical point appears (see Fig. 3). According to the results by Eisenschitz[12)], Sato[13)] and Nagamiya[14)], the temperature dependence of the order parameter is appreciably affected by taking into account the anomalous thermal expansion accompanied

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[12)] R. Eisenschitz, *Proc. Roy. Soc.*, **A168**, 546 (1938).
[13)] Y. Sato, *J. Phys. Soc. Japan*, **2-1**, 17 (1947).
[14)] T. Nagamiya, "Kotai-ron (Solid State Physics)", 1, Kyōritsu, Tokyo (1951), p. 20.

with the order-disorder phase transition in the case of binary alloy systems. We have then attempted to examine the effect of volume change in the present case as the next stage of refinement. After Sato's treatment, we can get the following expression for the abnormal expansion coefficient

$$\begin{aligned}\Delta\alpha=\alpha(s)-\alpha(0)&=\kappa_0 \mathrm{d}s^2/\mathrm{d}T\cdot E_0\mathrm{d}(E/E_0)/\mathrm{d}V\\ &=\kappa_0 \boldsymbol{R}T_c/2\cdot \mathrm{d}s^2/\mathrm{d}T\cdot \mathrm{d}(E/E_0)/\mathrm{d}V \qquad (7)\end{aligned}$$

Here, κ_0 is isothermal compressibility of the disordered phase; V the molar volume; E and E_0 the ordering energy at T°K and 0°K, respectively. Then, the abnormal expansion over V°, the molar volume at 0°K, is given by

$$v=\int_0^T V^0\Delta\alpha \mathrm{d}T=\int_1^s V^0 C\mathrm{d}s^2=-CV^0(1-s^2) \qquad (8)$$

where the following abbreviations were used

$$\mathrm{d}(E/E_0)/\mathrm{d}V=B, \qquad B\boldsymbol{R}T_c=C$$

By using the observed $v_{\max}$ value 0.41 cc./mol. and $V_0=110$ cc.*, C becomes -3.76×10^{-3}.

Based on these expressions the following thermodynamic functions are derived as functions of s, v and T.

$$U(s,\ v,\ T)=E_0-Es^2=E_0\{1-(1+Bv)s^2\} \qquad (9)$$

$$\begin{aligned}G(s,\ v,\ T)=&E_0\{1-(1+Bv)s^2\}\\ &+\boldsymbol{R}T/2\{(1+s)\ln(1+s)+(1-s)\ln(1-s)\\ &-2\ln 2\} \qquad (10)\end{aligned}$$

Here, G is the Gibbs free energy**. From $\partial G/\partial s=0$ and $\partial^2 G/\partial s^2=0$, we have

$$s=\tanh 2E_0 s\{(1+Bv)+BCV_0 s^2\}/\boldsymbol{R}T \qquad (11)$$

$$\boldsymbol{R}T_c/E_0=2(1+Bv_{\max}) \qquad (12)$$

The differentiation of $U(s,\ v,\ T)$ with T gives an expression for excess heat capacity over that arising from lattice vibration. The maximum value is obtained from the limitation of $s\to0$.

$$\begin{aligned}C_{\max}&=\lim_{s\to0}(\partial U/\partial s)/(\partial T/\partial s)\\ &=3\boldsymbol{R}/2\{1-(6BCV_0)/(1+Bv_{\max})\}^{-1} \qquad (13)\end{aligned}$$

On the assumption that the $C_{\max}$ value thus defined is identical with the experimentally observed ΔC_p, the following set of values can be obtained: $B=-2.44\times10^{-1}\ \mathrm{cc}^{-1}$, $\kappa_0=1.25\times10^{-6}\ \mathrm{atm}^{-1}$. By using these numerical values and the observed volume change, the refined $\Delta\beta-T$ curve is calculated and drawn by the full line in Fig. 8, where a fairly satisfactory agreement between this curve and the observed points is seen. It is to be noted that the calculated total entropy change 1.06 e. u. (from −70 to +35°C) is in good agreement with the observed one 1.10 e. u., if the same numerical values for parameters are used. The value of κ_0 obtained above seems to be somewhat smaller for this kind of crystal including organic complex ion, since the compressibility is in the range of $(2\sim7)\times10^{-6}\ \mathrm{atm}^{-1}$ for usual ionic crystals. Although the model proposed here is merely a possible one, it may be said that rather satisfactory results were obtained.

A preliminary study of proton magnetic resonance absorption of the powdered specimen of this crystal was recently made by Yamagata* over the temperature range between −190 and +40°C and there was no detectable change in the line width at the critical point. The observed second moment 8.35 Gauss^2 almost coincides with 7.82 Gauss^2 of the calculated value obtained by assuming the isolated -NH_3^+ group (the value 1.032 Å for N–H distance and tetrahedral angle were assumed) with rotational flipping motion about the C–N axis. The situations are very similar in the cases of ammonium halides[15].

Summary

Measurements of the heat capacity (−80∼+60°C) and the thermal expansion (−40∼+60°C) of aniline hydrobromide were carried out covering the transition temperature which has been observed recently by X-ray methods. The observed heat capacity versus temperature curve was of the λ-shape, similar to that of the order-disorder phase transition of binary alloy systems. The following results were obtained; T_c (the temperature corresponding to the heat capacity peak) 22°C, ΔH (heat of transition, −70∼+35°C) 297±10 cal./mol., ΔS (entropy of transition, the same temperature interval) 1.10±0.05 e. u., ΔC_p (drop of heat capacity at T_c)∼9 cal./mol. deg. Also the anomalous behavior of thermal expansion was observed in the vicinity of the critical temperature. These observations showed that the transition was of higher order nature.

Based on the lits of knowledge of the crystal structures above and below the critical temperature, the author has discussed the main feature of the phase transition from the sandpoint of the orientational order-disorder of the -NH_3^+ ionic group and obtained fairly satisfactory results.

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* This value was taken from $d_{25}=1.58$, by the picnometric measurement of Taguchi et al.[1]

** The G function expressed here does not correspond exactly to the Gibbs free energy, since the PV term was neglected.

* Private communication.

15) H. S. Gutowsky, G. E. Pake and R. Bersohn, *J. Chem. Phys.*, **22**, 643 (1954); R. Bersohn and H. S. Gutowsky, ibid., **22**, 651 (1954).

The author wishes to express his sincere thanks to Professor I. Nitta, Professor T. Watanabe and Dr. I. Taguchi for their valuable advice and continued interest in the present study, to Professor T. Nagamiya for his valuable suggestion, and to Professor S. Seki for his kind guidance and illuminating discussion. He is also grateful to Dr. H. Chihara for his kind support, and to Mr. K. Nakatsuka for his technical assistance.

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