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Phase Transition of $SnCl_2(H_2O)_x(D_2O)_{2-x}$ as Studied by High Resolution Heat Capacity Measurement

Masami Tatsumi, Takasuke Matsuo, Hiroshi Suga, and Syûzô Seki*
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

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The previously published heat capacity data on $SnCl_2(H_2O)_x(D_2O)_{2-x}$ (x=2.00, 1.97, 1.75, 1.50, 0.96, 0.50, 0.25, 0.03) were analyzed to derive anomalous contribution due to the phase transitions that occur between 218 and 235 K depending on the isotopic composition. The phase transition is of the first-order for x=2.00, 1.97, and 1.75. The entropy discontinuities at the transitions are (0.149±0.005), (0.152±0.005), and (0.133±0.010) $J K^{-1} mol^{-1}$, respectively, out of the total transition entropies of 3.98, 3.90, and 3.89 $J K^{-1} mol^{-1}$. The first-order transition does not occur for the other crystals for which the heat capacity anomaly is rounded. Apparent critical exponent α of the heat capacity was calculated for all of the crystals. They are in the range from 0.43 to 0.80 and have the same value below and above the transition temperature for each of the crystals in agreement with the spatial two dimensionality of the crystal structure. No evidence was found for crossing-over to the three dimensional ordering. Change of the transitional behavior with the isotopic composition was discussed in analogy with the liquid-vapor critical phenomenon. An argument based on the crystallographic symmetry of the actual crystal and the corresponding dimer lattice was advanced for this interpretation of the unusual isotope effect.

In the previous paper[1)] we reported on the high resolution measurement of the heat capacity of the solid solution system $SnCl_2(H_2O)_x(D_2O)_{2-x}$ in which the heat capacity was measured from 10 to 300 K with an adiabatic calorimeter that is capable of measurement with a temperature step smaller than 10 mK. We obtained the following result from the measurement. The phase transition temperature defined as the temperature of the entropy discontinuity or, in case of absence of the discontinuity, as the temperature of the maximum of the heat capacity, increased smoothly from 218.0 to 234.6 K as the deuterium content increased from the natural abundance to 98.5%. The anomalous heat capacity became broader at the same time. Small first-order transition portion was found in the hydrogen-rich solid solutions, x=2.00, x=1.97, and x=1.75. In order to reveal their differences, the anomalous heat capacities are displayed in Fig. 1 as a function of reduced temperature T/T_c. Increasing the proton concentration x tends to increase sharpness of the anomalous heat capacity. The heat capacities of x=2.00 and x=1.97 and also x=1.50, x=0.96, x=0.50, and x=0.25 lie on the same smooth curves, respectively.

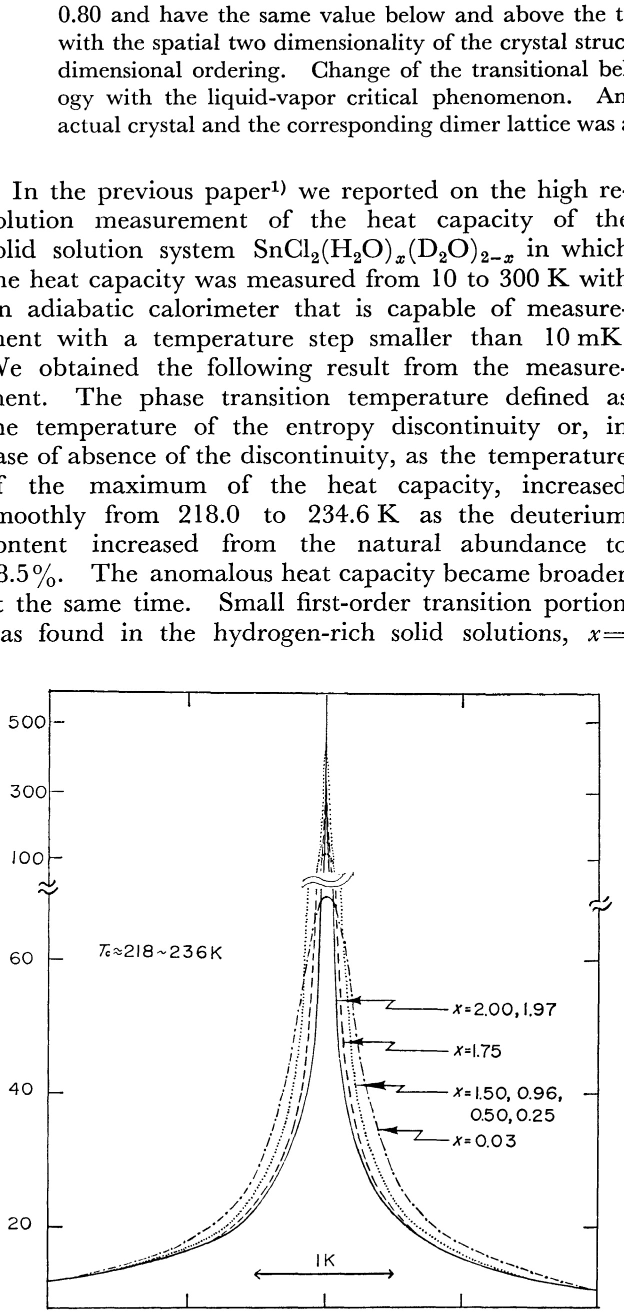


Fig. 1. Anomalous heat capacity (ΔC_p) *versus* reduced temperature (T/T_c).

Annealing effect was found in the crystal with x=0.96 (annealing period; two years), but not for x=0.50 (ten months) and x=0.03 (four years). The difference in the annealing behavior is due partly to the difference in the time intervals between the crystal preparation and the first measurement and partly to the difference in the isotopic composition. Naturally one does not expect much inhomogeneity in the x=0.03 crystal because only 1.5% of the deuterium is replaced by hydrogen. It will be significant that this crystal exhibits extensive rounding while the conjugate crystal (x=1.97) has a first-order transition without any rounding. Thus, inhomogeneous distribution of the isotopes did contribute to the rounding but it was removed by annealing.

It was concluded that the first-order transitions in the hydrogen-rich crystals and the rounded heat capacity in the deuterium-rich ones are genuine equilibrium properties of the solid solutions. This conclusion will be corroborated later by the smooth and regular behavior of the entropy surface as a two-dimensional function of the temperature and the isotope composition. It is to be noticed in particular that the behavior of the crystal is asymmetric with respect to the substitution of deuterium for hydrogen. In this paper, we will analyse the heat capacity data with an emphasis on the isotope effect on the phase transition.

We showed in earlier papers[2—4)] that the first-order transition in $Cu(HCO_2)_2\cdot 4H_2O$ remains of the first-order when the H_2O is replaced by D_2O, and the second-order transition in $K_4Fe(CN)_6\cdot 3H_2O$ remains to be second-order after similar substitution. The isotope effects on the transition temperature are of the same magnitude for these three substances and are much smaller than in *e.g.* KH_2PO_4 where tunneling motion of the proton is incorporated. Disappearence of the first-order transition is thus the most unique aspect of the isotope effect in this solid solution system.

Salinas and Nagle[5] reported a statistical mechanics of the phase transition of $SnCl_2 \cdot 2H_2O$ (TCD), using the isomorphism between the proton distribution allowed by the Bernal-Fowler ice condition and close-packed dimer distribution on the 4—8 lattice. The theory succeeded in predicting the correct ground state configuration of the proton arrangement and reproducing the symmetrical heat capacity anomaly characteristic of the two-dimensional system. However, quantitative prediction of the theory—logarithmic divergence of the heat capacity— was not supported by the experiment.

Determination of the Critical Parameters. The heat capacity C is assumed to have the asymptotic form near the critical temperature T_c,

$$C = (A/\alpha)(|t|^{-\alpha}-1)(1+D|t|^{\beta}) + B + Et, \qquad (1)$$

where

$$t = (T-T_c)/T_c$$

is the reduced temperature. The parameters A, B, D, E, α, β are allowed to take different values above and below T_c. In the latter case, the primed notations are used. The term $(A/\alpha)|t|^{-\alpha}$ represents the leading contribution to the singularity of C. The positive value of α corresponds to a heat capacity diverging to infinity. The smaller the magnitude of α, the sharper the heat capacity becomes and it is called weaker divergence. Negative value of α corresponds to a cusped singularity where the heat capacity curve has an infinite slope but finite value. In the case of $\alpha=0$, there are two possibilites. One is the logarithmic divergence and the other a finite discontinuity. $D|t|^{\beta}$ is the correction term which represents a singular contribution that vanishes at T_c. The lattice contribution to the heat capacity is expressed by the last two terms, $B+Et$, where the constant B may contain a contribution associated with the phase transition.

We calculated the critical exponents from the experimental data in the range of $|t| \leq 10^{-2}$. The first-order phase transition and rounding were excluded from the fitting. The discontinuous increase of the entropy at the first-order transition is about 4% of the total transition entropy and was disregarded for this purpose.

To simplify the fitting procedure, we imposed several constraints. We assumed that the correction term is negligible, $D=D'=0$. The lattice contribution in Eq. 1 was assumed to be smooth through the transition. This assumption should be more legitimate for this crystal than is usual for other crystal because there is no major change in the crystal structure at the transition.[6] We put $E=E'$ and $B=B'$. The latter term includes the quantity $-A/\alpha$. Thus the final form used in the fitting is

$$C = (A/\alpha)|(T-T_c)/T_c|^{-\alpha} + B + ET. \qquad (2)$$

The terms B and E in this equation have slightly different meaning from that in Eq. 1. Determination of the lattice terms $B+ET$ is discussed in appendix II.

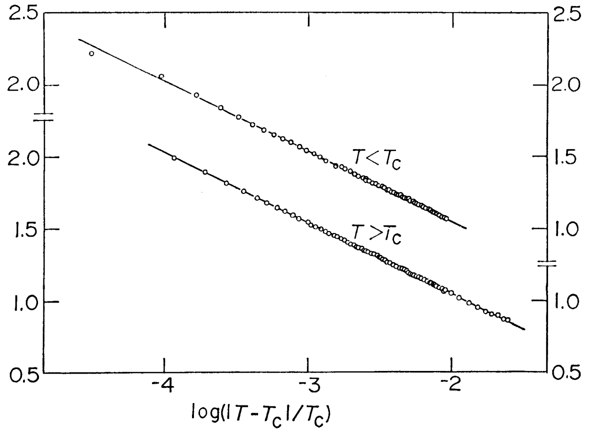


Fig. 2. Logarithmic plot of the anomalous heat capacity of $SnCl_2(H_2O)_{2.00}(D_2O)_0$.

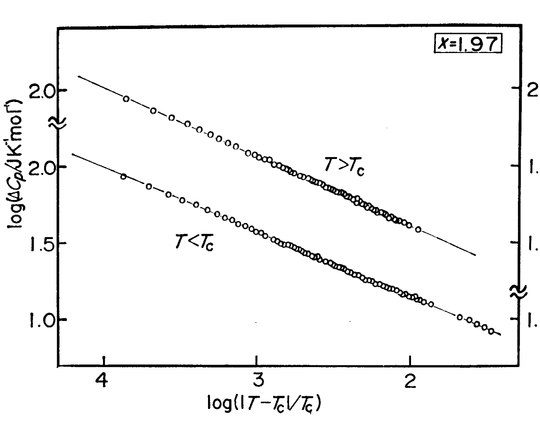


Fig. 3. Logarithmic plot of the anomalous heat capacity of $SnCl_2(H_2O)_{1.97}(D_2O)_{0.03}$.

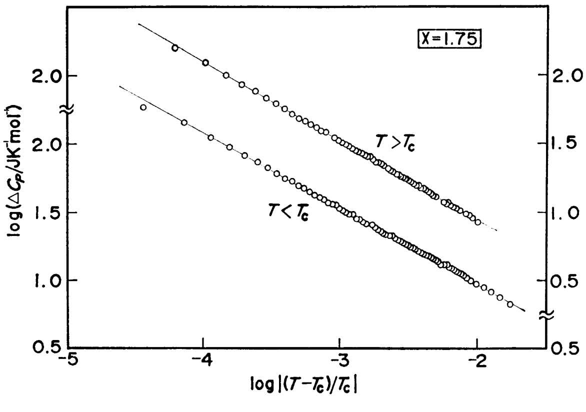


Fig. 4. Logarithmic plot of the anomalous heat capacity of $SnCl_2(H_2O)_{1.75}(D_2O)_{0.25}$.

The $\log\{C_p-(B+ET)\}$ was plotted as a function of $\log|(T-T_c)/T_c|$ for various values of T_c and B. The best combination was chosen with the linearity of the plot as the measure of the good fit. Combined uncertainty in α due to uncertainty in determining T_c and the lattice heat capacity would be about 5% of its value.

For $|t| > 10^{-2}$, the plot deviated from Eq. 2. This may imply that contribution from the higher

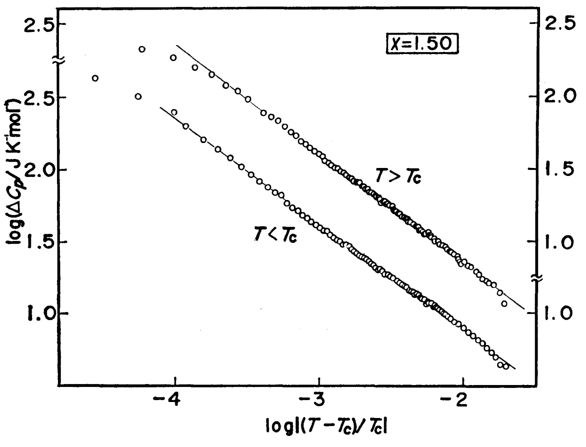


Fig. 5. Logarithmic plot of the anomalous heat capacity of $SnCl_2(H_2O)_{1.50}(D_2O)_{0.50}$.

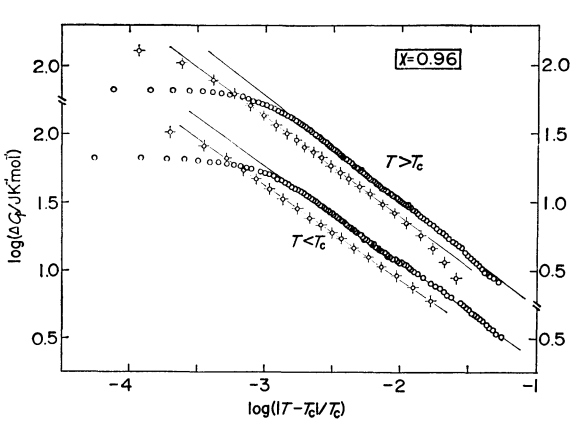


Fig. 6. Logarithmic plot of the anomalous heat capacity of $SnCl_2(H_2O)_{0.96}(D_2O)_{1.04}$. ○: $x=0.96$, -⌽- : $x=0.96$(II).

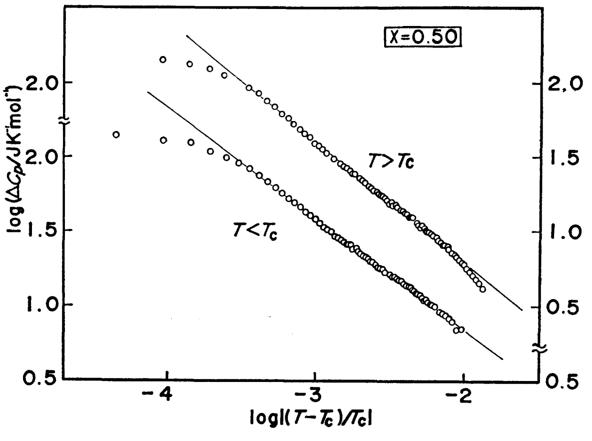


Fig. 7. Logarithmic plot of the anomalous heat capacity of $SnCl_2(H_2O)_{0.50}(D_2O)_{1.50}$.

order correction terms is significant and/or that the lattice heat capacity deviates from the assumed linearity in T. This is not a serious problem as far as determination of α is concerned. Figures 2—9 show the logarithmic plots for the crystals $x=2.00$ to 0.03. The plot for $x=2.00$ is reproduced here for the sake of completeness.[7]

Rounding of the anomalous heat capacity and hence deviation of the logarithmic plot from the linearity in the small $|t|$ region occurs for the crystals $x=1.50$, 0.96, 0.50, 0.25, and 0.03. The rounding of the first crystal is limited to $|t|<10^{-4}$ and those of the second, third, and fourth were to $|t|\leq 3\times10^{-4}$. The last crystal had a wider rounding region $|t|\leq 10^{-3}$. It is interesting to remember that in most magnetic transitions a larger rounding region occurs below T_c than above. Heller[8] pointed out that this may be an intrinsic effect related with the formation of domain structure. The rounding in the present crystal occurs in the same temperature interval on both sides of the transition temperature and cannot be due to a domain structure.

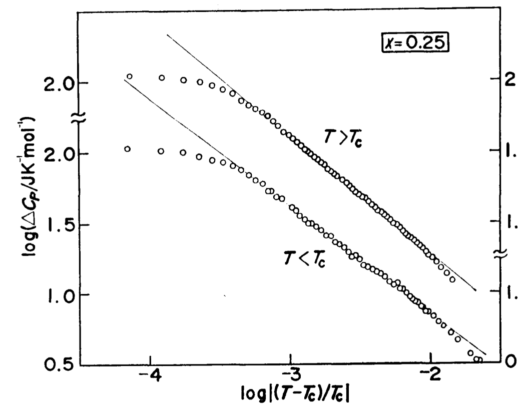


Fig. 8. Logarithmic plot of the anomalous heat capacity of $SnCl_2(H_2O)_{0.25}(D_2O)_{1.75}$.

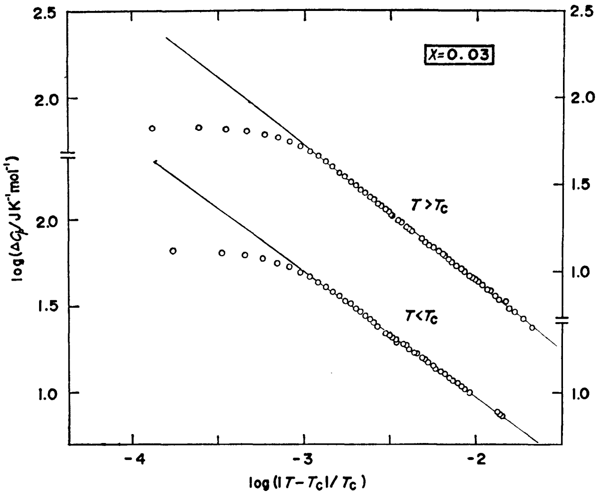


Fig. 9. Logarithmic plot of the anomalous heat capacity of $SnCl_2(H_2O)_{0.03}(D_2O)_{1.97}$.

We attempted to interpret the rounding on an assumption that the crystal behaves as if it were composed of microcrystals which have distributed transition temperatures.[9] The heat capacity of the entire crystal is then given by

$$C(T,\ T_c) = \sum_i C(T,\ T_{ci})f(T_c,\ T_{ci})/\sum_i f(T_c,\ T_{ci}), \qquad (3)$$

where $C(T,T_{ci})$ is the heat capacity at T of a microcrystal having the transition temperature T_{ci}. This is assumed to have the form of Eq. 2. $f(T_c,T_{ci})$ is the distribution function of the critical temperature T_{ci} and assumed to be gaussian centering at T_c.

Table 1. Summary of critical parameters

	T_c/K	α'	α	α'/α	A' / J K^{-1} mol^{-1}	A / J K^{-1} mol^{-1}	A'/A	$C_{p_{max}}$ / J K^{-1} mol^{-1}	S_∞ / J K^{-1} mol^{-1}
x=2.00	218.01	0.492	0.492	1.000	0.568	0.565	1.005	∞	3.98
x=1.97	218.22	0.434	0.451	0.962	0.793	0.720	1.101	∞	3.90
x=1.75	219.96	0.573	0.579	0.990	0.389	0.354	1.099	∞	3.89
x=1.50	221.88	0.731	0.757	0.966	0.200	0.168	1.192	571	4.02
x=0.96	225.92	0.720	0.765	0.941	0.287	0.233	1.228	214	—
x=0.96(II)	225.89	0.696	0.733	0.950	0.238	0.194	1.225	295	4.05
x=0.50	229.15	0.747	0.785	0.952	0.165	0.134	1.230	306	3.86
x=0.50(II)	229.14	—	—	—	—	—	—	316	—
x=0.25	230.92	0.753	0.754	0.999	0.168	0.134	1.251	269	3.95
x=0.03	234.64	0.730	0.778	0.938	0.228	0.170	1.341	226	4.02
x=0.03(II)	234.64	—	—	—	—	—	—	231	—

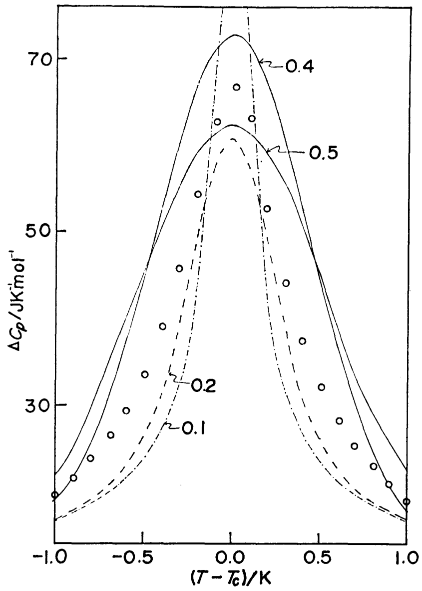


Fig. 10. Comparison of the experimental heat capacity with the model calculation assuming gaussian distribution of T_c. The numbers are the values of adjustable parameter corresponding to the half-width d of the gaussian distribution.

Some of the results for x=0.96 are shown in Fig. 10. Evidently the fit is very poor. A similar attempt[10] on KDP was also reported to be unsuccessful. If one wishes to save the model of the distributed transition temperature, one would have to modify Eq. 2 and/or Eq. 3. Modification of Eq. 2 is not acceptable because it describes the heat capacity of the x=2.00 crystal accurately. On the other hand, it is impossible to refute every modification of the distribution function in Eq. 3. However, so far as the model was applicable at all, it was applicable with the gaussian distribution.[11]

It will not be fruitful to look for the distribution function that reproduces the experimental result. Distributed T_c implies, as an underlying picture, quenched distribution of chemical or physical impurities and inhomogeneities in the crystal. In view of the manner in which the eight crystals were prepared, the only possibility is the inhomogeneity of the isotope distribution. This inhomogeneity was leveled off by annealing (see Ref. 1). It is important to note that occurrence of the phase transition contradicts the assumption of quenched distribution of the isotopes. The phase transition occurs because the protons (or deuterons) jump around in the hydrogen bonded layer, not just among a few localized states. We conclude that the model of distributed transition temperature is not appropriate for the present crystal.

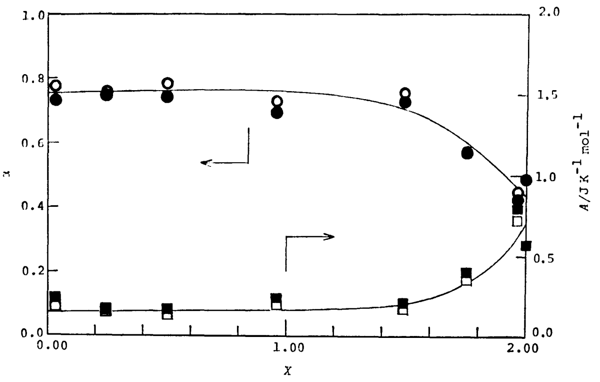


Fig. 11. Composition dependence of the critical parameters. ●: α', ○: α, ■: A', □: A.

Recently, it was suggested from dielectric measurement[12,13] that TCD shows a cross-over from two to three dimensional ordering around $t=10^{-3}$. However, the logarithmic plot of the heat capacity is smooth without any irregularity. This is true not only for the x=2.00 crystal but also for all of the other crystals except the x=0.03 crystal for which the rounding extends out to this region.

The critical parameters thus determined are given in Table 1 and Fig. 11. The critical exponent has the same value below and above T_c as expected from the symmetric shape of the heat capacity curves. In the region where the rounding is appreciable, physical meaning of the critical exponent is not clear because the region of small t where Eq. 2 is expected to be most appropriate is excluded from the fitting. However, the logarithmic plot is on a straight line over more than a decade of $|t|$ even for the most rounded case. Its physical meaning will be hopefully understood in future. The α values are in the range 0.43—0.8. They are much larger than typical value for magnetic systems. Comparable magnitude of α are

TABLE 2. SOME GRADUAL PHASE TRANSITIONS

Substance	T_c/K	ΔS/J K^{-1} mol^{-1}	ΔS_{jump}/J K^{-1} mol^{-1}	$\Delta S_{\mathrm{jump}}/\Delta S$	Ref.[a]
KH_2PO_4	121.71	3.33	0.379	0.114	(a)
KD_2PO_4	219.62	3.80	2.001	0.527	(b)
TlH_2PO_4	229.76	1.80	0.25	0.14	(c)
KH_2AsO_4	96.15	4.2	3.1	0.75	(d)
KD_2AsO_4	161.02	4.2	3.5	0.84	(d)
CsH_2AsO_4	146.23	4.4	2.7	0.61	(e)
NH_4HgCl_3	54.97	5.6	1.1	0.20	(f)
ND_4HgCl_3	58.26	5.7	1.2	0.21	(f)
$SnCl_2 \cdot 2H_2O$	218.01	3.98	0.149	0.0374	present study
$SnCl_2(H_2O)_{1.97}(D_2O)_{0.03}$	218.22	3.90	0.152	0.0390	present study
$SnCl_2(H_2O)_{1.75}(D_2O)_{0.25}$	219.96	3.89	0.133	0.0342	present study
$SnCl_2(H_2O)_{1.50}(D_2O)_{0.50}$	221.88	4.02	0.00	0	present study

a) (a) Ref. 10, (b), Ref. 14, (c) T. Matsuo and H. Suga, *Solid State Commun.*, **13**, 1829 (1973), (d) C. W. Fairall and W. Reese, *Phys. Rev. B*, **6**, 193 (1972), (e) M. Deutsch and E. Litov, *Ferroelectrics*, **7**, 209 (1974), (f) H. Kitano, Master's Thesis; Osaka University (1977).

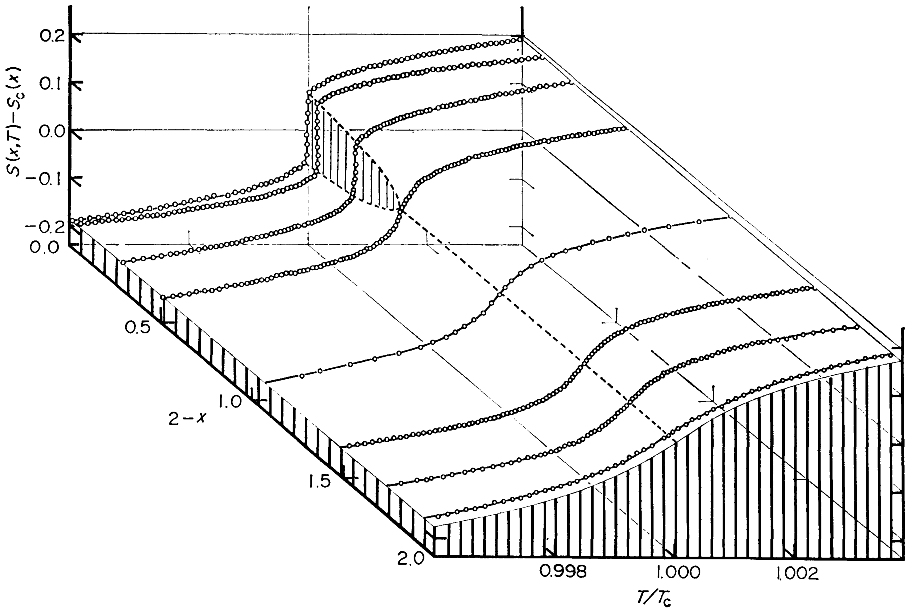


Fig. 12. Anomalous entropy of $SnCl_2(H_2O)_x(D_2O)_{2-x}$ *versus* temperature and isotopic composition.

found in KDP,[10] DKDP,[14] NH_4Cl,[15] NH_4Br,[16] and $NaNO_2$.[17] The crystals with $x=2.00$ and $x=1.97$ resemble KDP with respect to the value of α and occurrence of the first-order phase transition, but do not exhibit the logarithmic singularity which KDP[18] does. This indicated that dominant interaction in TCD is strong short-range forces that express themselves as the ice condition.

Order of the Phase Transition and Entropy Change near the Transition Temperature. It is often noticed that thermal equilibrium in the crystal is attained very slowly at a first-order transition. This is usually attributed to slow progress of the first-order transition. In the present study, slow equilibration was observed in the crystals with high hydrogen content. At the transition temperature of the crystals of $x=2.00$, 1.97, and 1.75, the equilibration time was 5—7 times as long as those in the normal temperature region. Such anomalous equilibration behavior was not found in the crystals with $x=0.96$, 0.50, 0.25, and 0.03. The crystal $x=1.50$ was the boundary case where the long equilibration time was observed only at one point of the measurement at the peak of the transition. A more quantitative evidence of the change in character of the phase transition with increasing deuterium content is shown in Fig. 12 as the anomalous entropy plotted as a function of the temperature and the isotopic composition. The surface was calculated by integration of the anomalous heat capacity divided by T. Evidently the transition is of the first-order for $x=2.00$, 1.97, and 1.75. The entropy discontinuities for these three crystals are (0.149 ± 0.005), (0.152 ± 0.005), and (0.133 ± 0.010) J K^{-1} mol^{-1}, respectively. The crystal with $x=1.50$ did not show distinct jump, but as noted above its equilibration behavior was similar to that of the crystal with the first-order transition. Thus $x=1.50$ corresponds to the critical composition where the first-order transition disappears.

We shall change subject for a while to the problem of classification of phase transitions. A phase transition is of the n'th order if the n'th derivative of the free energy is discontinuous at the phase transition. This is the classification due to Ehrenfest. Discontinuity in the higher-order derivative is not easy to detect experimentally. Therefore, phase transitions which are not of the first-order are classified collectively as the higher-order. This classification is not general enough to be applicable to all of the phase transitions, since it does not contain the divergent anomalies.

In another classification, a phase transition is called isothermal if it occurs at a fixed temperature, and gradual if the anomaly occurs over a range of temperature. An isothermal transition is of the first-order, but gradual transition can be of the first-order, higher-order or divergent type. This classification is more convenient than the first classification, because gradual first-order transitions are more closely related to higher-order and divergent transitions than to the strictly first-order transitions. The first-order transitions are divided into strongly first-order and weakly first-order.

As a quantitative measure of the strength of the "first-orderedness," we propose the entropy discontinuity divided by the total transition entropy. Thus the fusion of a pure substance is a strongly first-order transition because all of the entropy change occurs at the melting temperature. In Table 2 we collected some of the weakly first-order transitions of ferroelectric and related substances including the present crystals. It is interesting that, so far as is known, magnetic transitions are rarely of weakly first-order. It should be added that we singled out the entropy from among other thermodynamic quantities that may possibly behave anomalously at the transition. This is because this quantity is amenable to direct experimental measurement irrespective of the atomic mechanism of the transition so far as we choose the temperature as the independent variable.

Comparison with the Dimer Model Calculation. Salinas and Nagle[5] gave an expression for the internal energy of the dimer model. We calculated the heat capacity C from the energy U,

$$C = \mathrm{d}U/\mathrm{d}T. \qquad (4)$$

The explicit expression is too lengthy to be reproduced here. For the sake of checking the calculation, we computed S_∞ numerically from the equation

$$S_\infty = \int_0^\infty (C/T)\mathrm{d}T, \qquad (5)$$

using the heat capacity given above. The result agreed with the direct calculation[19] given earlier, $S_\infty/R = 0.3769956\cdots$. Figure 13 compares the experimental heat capacity with the dimer model calculation. The calculated heat capacity is too sharp, corresponding to the logarithmic divergence as noted by Salinas and Nagle.[5] However, agreement between the experiment and the theory is excellent at 150 K where the glass transition (see Appendix I) allowed determination of the lattice heat capacity without ambiguity. The experimental entropy at $T = T_c$ and $T = 2T_c$ are (3.00 ± 0.12) and (3.94 ± 0.23) J K^{-1} mol^{-1}, respectively, for the $x = 2.00$ crystal. These are compared with the dimer model calculation $S(T_c) = 2.34$ and $S(2T_c) = 3.02$ J K^{-1} mol^{-1}.

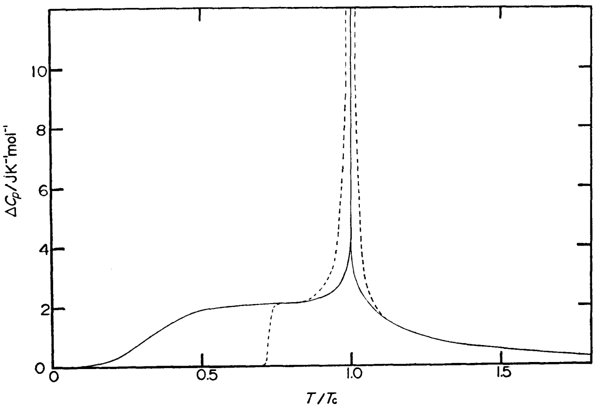


Fig. 13. Comparison of the heat capacity of $SnCl_2 \cdot 2H_2O$ with the dimer model calculation.

Problem of Tricritical or Bicritical Phenomenon. In this section we are concerned with interpretation of the disappearance of the first-order transition in the deuterium-rich crystals. In order to be sufficiently general, we consider a phase diagram in three dimensions.[20] A first-order phase transition is described by a coexistence surface in the space. The coexistence surface may terminate in following ways. i) The coexistence surface intersects another coexistence surface in a triple line at which three phases are in equilibrium. ii) The coexistence surface passes into another surface which continues to separate two phases but which has the property that all extensive variables are continuous at the surface. iii) The coexistence surface terminates in a line of critical point. In the two dimensional phase diagram, these three correspond to i) triple point, ii) tricritical point and iii) bicritical point. Our result corresponds to ii) or iii).

a) Tricritical Point: The three axes in the phase diagram are temperature T, the field η conjugate to the order parameter and a secondary variable ζ. η is often a fictious field uncontrollable in the laboratory. For instance we have no direct means of controlling the orientational order of the ammonium ion in NH_4Cl crystal. ζ is taken as a controllable variable such as pressure, magnetic field or chemical potential. The phase diagram looks schematically like Fig. 14. The three curves meeting at the tricritical point represent

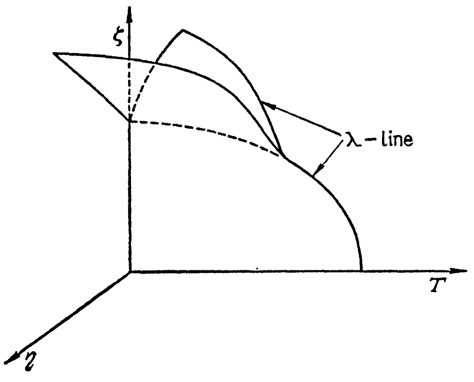


Fig. 14. Schematic phase diagram of a system with a tricritical point.

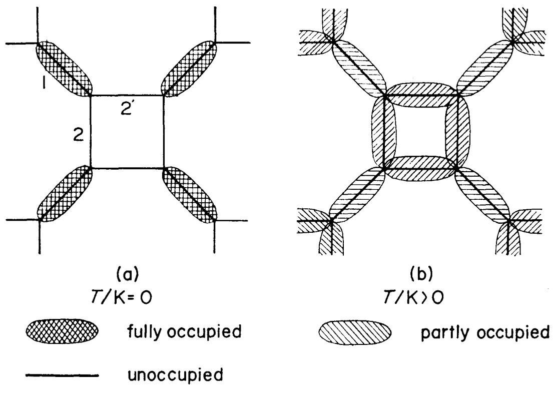
lines of the critical point. The three coexistence surfaces meets in a line of triple point represented by the broken line. The surface at $\eta=0$ is the coexistence surface of the positively and negatively ordered phases.

The behavior of $SnCl_2(H_2O)_x(D_2O)_{2-x}$ appears to fit in well with the phase diagram if one identifies the ζ axis with the isotopic concentration. The first-order transition line (the broken line) disappears as the tricritical point is approached by changing the ζ value.

However, there is a difficulty in this correspondence arising from the peculiarity of this crystal. We cannot define order parameters because the symmetry of the two phases involved are the same. Therefore, it is impossible to define its conjugate field η.

In order to illustrate the point, we shall take NH_4Cl as an example. The two phases coexisting on the surface $\eta=0$ are related with each other by changing the orientation of all the ammonium ions by 90° relative to the crystal axis. In the disordered phase this produces an equivalent state. Such an operation is not possible in TCD. A proton in the crystal occupies one of the seven sites but none of them are equivalent with each other. Tricritical points have been discussed in NH_4Cl,[21] ND_4Cl,[22] NH_4Cl–NH_4Br,[23] and other systems where a first-order transition changes to a higher-order one as an external parameter changes. The same argument can not be applied in the present case in spite of the similarity of the thermodynamic behavior.

b) Bicritical Point and Super Critical State: This type of critical point always exists in a simple liquid-vapor system. If one chooses an appropriate path in the pressure-temperature plane, one can obtain vapor phase from the liquid phase without discontinuity. This is possible because the vapor and liquid have the same spatial symmetry.[24] The same would be true in the crystalline state. Non-existence of the critical point between liquid and crystal was rationalized by the same argument.[24] In the case of TCD, Kiriyama *et al.*[25] showed that the space group $P2_1/c$ and the unit cell size remain the same as the crystal undergoes the phase transition. This is a very peculiar property of this crystal, since change of symmetry is believed to be the most essential characteristic of solid state phase transitions in general. On the other hand, thermodynamic property of this phase change is also unusual. As shown in Fig. 12 the first-order transition disappears at $x\simeq1.5$, beyond which the heat capacity is rounded and genuine singularity does not occur any more. This behavior is similar to that of a simple liquid-vapor system at least qualitatively. The region $x\geq1.5$ where the first-order transition occurs corresponds to subcritical region and the region $x<1.5$ to the supercritical region.



(a) $T/K=0$

(b) $T/K>0$

Fig. 15. Dimer distribution at $T=0$ K (a) and $T>0$ K (b) on the 4—8 lattice.

Thus, two peculiarities of the phase transition in TCD, one crystallographic and the other thermodynamic, are interpreted coherently by an analogy with the liquid-gas critical point. At present, however, how the correspondence comes about between the isotope concentration in TCD and pressure in the liquid-vapor system is not understood.

It will be pertinent here to point out that a phase transition is possible at all between two phases of the same spatial symmetry. As an example we show in Fig. 15 a part of the dimer lattice studied by Salinas and Nagle.[5] Figure 15(a) shows the distribution of the dimers at 0 K where all of the dimer sites (1) and none of the (2) and (2′) are occupied. Two dimensional space group of this distribution is P4mm. At higher temperature, some of the dimers occupy the sites (2) and (2′) as shown in Fig. 12(b). This dimer distribution has the space group P4 mm again. Salinas and Nagle showed there is a phase transition between (a) and (b) in the sense that the thermodynamic function behaves singularly at a temperature determined by the energy of the dimer site (2) and (2′). It is evident that the low-temperature-phase is more ordered than the high-temperature-phase because it has a lower entropy. However we cannot define the order parameter for this lattice, since there is no symmetry breaking coordinate. Difficulty of defining order parameters in some dimer lattices was discussed also by Kasteleyn.[26] Thus, the dimer model gives some theoretical credential to the isomorphous transition found experimentally.

It is not clear how the nuclear mass influences the critical behavior of the hydrogen bonded system. It has been known that thermodynamic property of Ising model changes substantially if one assumes a distance-dependent coupling between the spins on a compressible lattice. Specifically, a first-order phase transition is possible if the lattice is sufficiently compressible.[27] It will be extremely interesting to investigate a compressible dimer lattice on the 4—8 lattice of Salinas and Nagle.

Conclusion

The heat capacity data discussed in the present paper was obtained with an adiabatic calorimeter using platinum and thermistor thermometers. High sensitivity of the thermistor allowed the heat capacity measurement close to the transition temperature without distorting the true temperature dependence of the anomalous heat capacity. Long term stability of the platinum thermometer and the resistance measuring apparatus enabled us to measure the heat capacity reproducibly over many years, which was essential for the investigation of the annealing effect. Adiabatic calorimetry rather than transient and temperature oscillation method was particularly suitable for studying the phase transition where thermal equilibration time was long at the transition temperature as in the present case. Use of the single crystals is also believed to be of essential importance not only in the thermal aspect but also for the homogeneity of the solid solutions. With these experimental set-up we believe that we have established the occurrence of a liquid-vapor type critical point in a crystalline substance for the first time.

Several problems are yet to be studied. We do not know physical meaning of the formal correspondence between the isotopic concentration in the present solid solution and pressure in the liquid-vapor system. This will be related to an equally interesting problem of phase transition in isotopic mixture in general. How can a phase transition temperature be defined accurately in the isotopically impure system? Position-exchangeability of the different isotopic atoms must be involved in this problem.

Finally, calorimetric and dielectric measurements at higher pressure will be informative for investigation of the critical behavior of the present system and are now in progress at the laboratory.

Appendix I. The Glass Transition

The glass transition is not a phase transition. It is a change from a non-equilibrium to equilibrium state. The glass transition in TCD occurs when, around 150 K, positional change of the protons (or deuterons) becomes so slow that they cannot find the equilibrium distribution within the experimental time. The glass transitions in normal and deuterated TCD were discussed in an earlier paper.[19] In this appendix we add some comments on the glass transition of the solid solutions.

Occurrence of the glass transition in TCD is a fortunate phenomenon for interpretation of the phase transition in two respects. First, we can be sure that the motion of the protons (or deuterons) at the phase transition temperature is rapid enough for their equilibrium distribution to be attained within the experimental time. For the phase transition occurs at much higher temperature than the glass transition. This is particularly important for the solid solutions because we can be sure that we are dealing with an annealed system rather than quenched one. Second, the glass transition allows experimental determination of the vibrational heat capacity below the glass transition temperature. This is a useful piece of information for separating the anomalous heat capacity from the total experimental heat capacity. Appendix II deals with this problem.

As the glass transition *per se*, the relaxational behavior deserves a comment. The heat capacity of the solid solutions around the glass transition and the glass transition temperature as a function of the composition were given in the previous paper. From the exothermic drift rate the relaxation time was determined by the method described previously[19] and plotted in Fig. A1. These figures show that the glass transition in $SnCl_2 \cdot 2D_2O$ occurs at ≈5 K higher than in $SnCl_2 \cdot 2H_2O$ and that the glass transition interval in the solid solutions is not broader than in the hydrate or deuterate crystal. This means that correlation region of the atomic motion is so large that the local isotopic concentration does not deviate from the average concentration. This supports the earlier discussion based on the structure of the hydrogen bond network that the smallest unit of the atomic motion consists of eight hydrogen atoms.

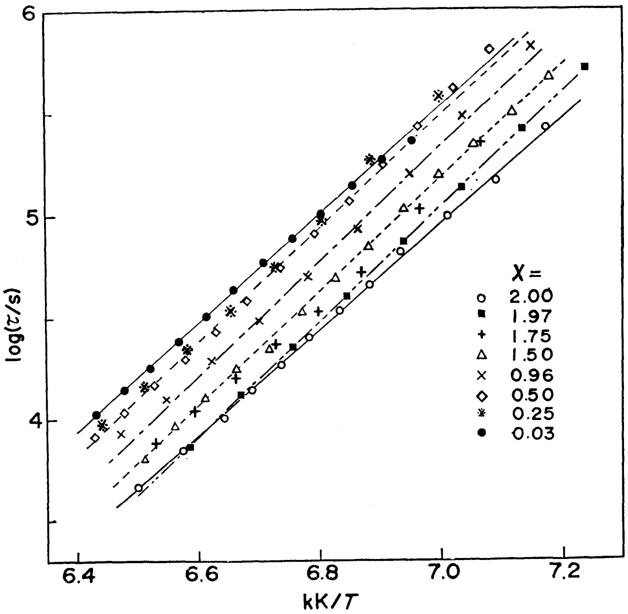


Fig. A1. Arrhenius plot of the enthalpy relaxation time of $SnCl_2(H_2O)_x(D_2O)_{2-x}$.

Appendix II. Determination of the Lattice Heat Capacity

It was found that the heat capacity jump at the glass transition is reproduced correctly by the dimer model using the experimental transition temperature as the only adjustable parameter. The dimer model calculation was assumed to be correct up to 190 K and above 250 K where the anomalous heat capacity is small again. The dimer model gave too small a heat capacity in the intermediate region involving the phase transition. Interpolation of the normal heat capacity into this region was facilitated by spectroscopic data.[28,29] The vibrational frequencies used are as follows. Internal vibration of the two water molecules: 3125, 2975, 1545, and 3505, 3375, 1610 cm^{-1}, librational modes of the two water molecules: 945, 853, 542, and 710, 486 and 415 cm^{-1}, internal and external vibrations of $SnCl_2 \cdot H_2O$: 323, 198, 134, 101, 67, 58, and 254, 250, 164, 139, 121, and 111 cm^{-1}.

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