The Phase Transition of Crystalline Potassium Thiocyanate, KSCN. II. X-Ray Study

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As has been illustrated in the foregoing paper[1], thermal and infrared absorption data suggest that the mechanism of the phase transition of potassium thiocyanate is described by a model of the order-disorder type transition for the orientation of the rod-shaped thiocyanate ion.

The aim of the present investigation is to confirm the above-mentioned mechanism of transition by the X-ray diffraction method, a proceeding based on the knowledge of the crystal structures below and above the transition temperature.

The crystal structure of the room temperature modification is known. According to Klug[2], potassium thiocyanate is isomorphous with D^{11}_{2h}–Pbcm, and its orthorhombic unit cell, containing four formula units, has the following dimensions:

$$a=6.66\text{Å},\ b=6.635\text{Å} \text{ and } c=7.58\text{Å}$$

Throughout this description, the axes (X, Y, Z) are derived from those of Klug (X', Y', Z') by a transformation: $X=Z'$, $Y=Y'$, $Z=X'$. A structure which gives a fairly good agreement between observed and calculated structure factors is obtained by putting atoms in the following equivalent positions given by D^{11}_{2h}–Pbcm.

4K:

$$u\ \frac{1}{4}\ 0,\ u\ \frac{1}{4}\ \frac{1}{2},\ \bar{u}\ \frac{3}{4}\ 0,\ \bar{u}\ \frac{3}{4}\ \frac{1}{2};$$

4C, 4N, 4S:

1) M. Sakiyama, H. Suga and S. Seki, This Bulletin, **36**, 1025 (1963).
2) H. P. Klug, *Z. Krist.*, **85**, 214 (1933).

$$v\ w\ \frac{1}{4},\ \bar{v}\ \bar{w}\ \frac{3}{4},\ v\ \frac{1}{2}-w\ \ \frac{3}{4},\ \bar{v}\ \frac{1}{2}+w\ \ \frac{1}{4};$$

with $u(\mathrm{K})\approx\frac{3}{4}$, $v(\mathrm{S})=0.385$, and $w(\mathrm{S})=0.125$. The suggested parameters for nitrogen are $v(\mathrm{N})=0.080$ and $w(\mathrm{N})=0.400$; for carbon, $v(\mathrm{C})=0.205$ and $w(\mathrm{C})=0.280$. The arrangement of the thiocyanate ions in the unit cell is shown in Fig. 1. All the thiocyanate ions are lying on planes parallel to (0 0 1) and are oriented to the face diagonals, as Fig. 1 shows. The infrared absorption lines referred above correspond to the bending vibrations of the

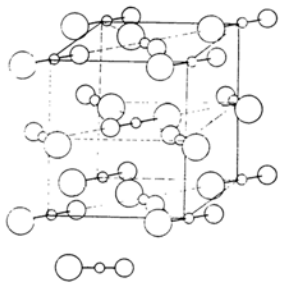

Fig. 1. The arrangement of thiocyanate ions in the low temperature phase.

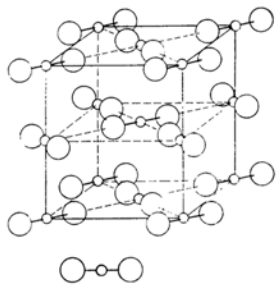

Fig. 2. The arrangement of thiocyanate ions in the high temperature phase.

thiocyanate ions in and out, respectively, of these planes.

The Crystal Structure of the High Temperature Phase

In order to investigate the crystal structure of the high temperature phase, X-ray diffraction experiments were carried out as follows:

The crystals used in the present experiments were obtained by slow evaporation from methanol solutions. In form they are thin rods elongated along [1 0 0]. By a preliminary test, it was found that the transition occurred in a single crystal. The crystals do not shatter on passing the transition temperature, and the process is almost completely reversible.

As the crystal is highly deliquescent, each sample was sealed in a thin, evacuated capillary. Hot air was blown in a constant stream over the capillary mounted on the goniometer in order to maintain the sample at a certain temperature between 160°C and room temperature. A thermocouple was placed at the nozzle of the jet. Before the crystal was set on the goniometer head, another thermocouple was mounted in place of the sample in order to estimate the temperature gradient in the hot air stream. As no appreciable difference was observed between the temperatures read by the two thermocouples, the temperature of the crystal was estimated by the thermocouple placed at the nozzle during the exposure.

Oscillation photographs were prepared by using [1 0 0] and [0 0 1] as the axes of rotation. Precession photographs for the $hk0$ and $hk1$ levels were also prepared.

The general appearance of the oscillation and precession photographs taken at 160°C was very like those taken at room temperature, indicating that the size of the unit cell and the arrangement of the constituent atoms do not change appreciably. However, the symmetry of the reciprocal lattice becomes ditetragonal and many of the weak reflections disappear, though the intensity of reflections from planes with the indices $hk1$ for $h+k+l$ even seems to be affected by the temperature factor alone. The lattice constants are found to be:

$$a=b=6.70\text{Å}\ \text{and}\ c=7.73\text{Å}\ \ (\text{at } 160^\circ\text{C})$$

To all the extinction rules observed for the room temperature modification, is now added hkl for $h+k+l$ odd. The space groups compatible with these rules are $C^{10}_{4v}-I4\,cm$, $D^{10}_{2d}-I\bar{4}c2$ and $D^{18}_{4h}-I4/mcm$.

Let us now try to derive a structure based upon these space groups, starting first with $C^{10}_{4v}-I4c2$. In this space group, there are two kinds of four-fold and one kind of eight-fold equivalent positions:

$$\left(0\,0\,0,\ \frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}\right)+$$

4a: $0\,0\,z,\ \frac{1}{2}\,\frac{1}{2}\,z;$

4b: $\frac{1}{2}\,0\,z,\ 0\,\frac{1}{2}\,z;$

8c: $x\,\frac{1}{2}+x\,z,\ \bar{x}\,\frac{1}{2}-x\,z,\ \frac{1}{2}+x\,\bar{x}\,z,$

$\frac{1}{2}-x\,x\,z$

Since there are four formula units in the unit cell, we have to find positions for four potassium, four carbon, four nitrogen and four sulfur atoms. Now, either 4a or 4b will give almost the same arrangement of potassium atoms as in the room temperature modification. However, the carbon, nitrogen and sulfur atoms cannot be placed on either 4a or 4b, because the length of the b-axis is too short to be accommodated with these atoms. Moreover, any one of these structures should give the natural decrease of intensities for $0\,k\,0$, e.g., $I_{020}>I_{040}>I_{060}>I_{080}$; this is not, however, the case. The only possibility of placing these atoms is to use 8c, with half a weight on each atom. If we place the potassium atoms on 4a, and the other atoms on 8c with appropriate parameters, we shall arrive at a structure which can easily be derived from the structure of the room temperature modification, the difference being that all the thiocyanate ions are here pointing statistically in two directions, namely, either [1 1 0] and $[\bar{1}\,\bar{1}\,0]$ or $[1\,\bar{1}\,0]$ or $[\bar{1}\,1\,0]$ (See Fig. 2). The same atomic arrangement can also be obtained either from $D^{10}{}_{2d}-I\bar{4}c2$ or $D^{18}{}_{4h}-I4/mcm$ by using 4a for potassium and 8h for the other atoms. If the origin of coordinates is shifted to $\frac{1}{4}\,\frac{3}{4}\,\frac{3}{4}$ from that given in International Table I, the positions of atoms can be given by:

$$\left(0\,0\,0,\ \frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}\right)+$$

4K in 4a:

$$\frac{3}{4}\,\frac{1}{4}\,\frac{1}{2},\ \frac{3}{4}\,\frac{1}{4}\,0,\ \frac{1}{4}\,\frac{3}{4}\,0,\ \frac{1}{4}\,\frac{3}{4}\,\frac{1}{2};$$

4C, 4N, 4S in 8c:

$$x\,x\,\frac{1}{4},\ \frac{1}{2}-x\,\frac{1}{2}-x\,\frac{1}{4},\ \frac{1}{2}+x\,\bar{x}\,\frac{1}{4},$$

$$\bar{x}\,\frac{1}{2}+x\,\frac{1}{4},\ \frac{1}{2}+x\,\frac{1}{2}+x\,\frac{3}{4},\ \bar{x}\,\bar{x}\,\frac{3}{4},$$

$$x\,\frac{1}{2}-x\,\frac{3}{4},\ \frac{1}{2}-x\,x\,\frac{1}{4},$$

with half a weight on each.

Comparing these coordinates with those assigned to the atoms in the room temperature modification, it can easily be understood that the structure factor for the high temperature modification has the same expression as those for the room temperature modification with the indices $h+k+1$, even if u(K) is taken to be 3/4 and $w_i=1/2-v_i$. The differences in these three structures given by $C^{10}{}_{4v}-I4cm$, $D^{10}{}_{2d}-I\bar{4}c2$ and $D^{18}{}_{4h}-I4/mcm$ lie in the fact that the site symmetry of the positions of the centers of the mass of the constituent ions corresponds to the following:

	$C^{10}{}_{4v}-I4$ cm	$D^{10}{}_{2d}-I\bar{4}c2$	$D^{18}{}_{4h}-I4/mcm$
K:	C_4-4	D_2-222	D_4-422
CNS:	$C_{2v}-mm$	D_2-222	$D_{2h}-mmm$

Since the thiocyanate ions are statistically disposed in two directions, or they flip from one direction to the reverse, there is no reason to assume that these thiocyanate ions have a symmetry lower than $D_{2h}-mmm$. The most probable space group is therefore, $D^{18}{}_{4h}-I4/mcm$. A fairly good agreement between observed and calculated structure factors was found with the following parameters: $x(C)=0.212$, $x(N)=0.110$, $x(S)=0.090$ and $B(\text{overall})=3.1\,\text{Å}^2$. Further refinement was not attempted because of the disordered structure. Though the crystal structure of potassium cyanate[3], KCNO, has not been worked out fully, it seems that it is isomorphous with the high temperature modification of potassium thiocyanate.

The Temperature Dependence of Ordering

It was observed that the intensity of the reflection from those crystal planes whose indices satisfy the relation, $h+k+l=2n+1$, decreases very rapidly as the temperature approaches the transition point. To investigate the temperature dependence of the intensity, the intensity of reflection (0 3 2) was measured at various temperatures by the scintillation-counter method, using monochromatized Mo-K_α radiation. The results are shown in Fig. 3, in which the scale of intensity is chosen arbitrarily. One of the reasons why this reflection was chosen for precise measurement is that there is only a negligible contribution

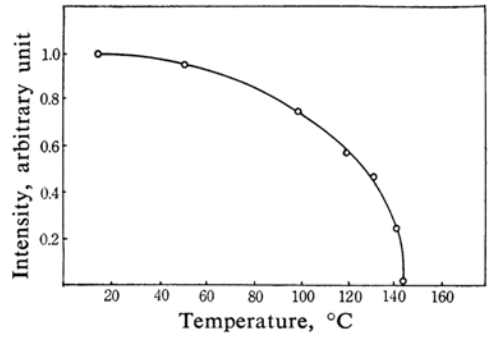

Fig. 3. Temperature dependence of intensity of (0 3 2) reflection.

3) S. B. Hendricks and L. Pauling, *J. Am. Chem. Soc.*, **47**, 2904 (1925); L. K. Frevel, *Z. Krist.*, **94**, 197 (1936); *J. Am. Chem. Soc.*, **58**, 779 (1936).

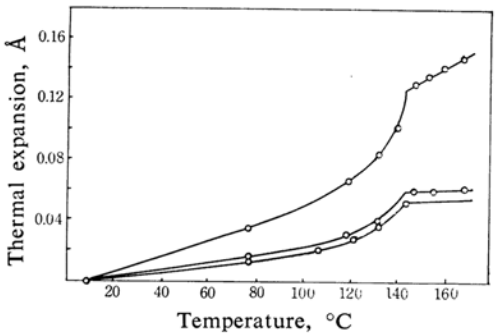

Fig. 4. Thermal expansion of lattice constants.

of the potassium atoms in its structure factor.

It was also observed that the lattice constants show an anomalous expansion near the transition temperature, a finding in accordance with dilatometric data given in the previous investigation. The results are shown in Fig. 4.

The temperature dependence of the reflected intensity directly gives information about the mechanism of the ordering of thiocyanate ions. If we call the arrangement of thiocyanate ions at room temperature "normal", the high temperature phase can be described as containing an equal number of the normal and of the reverse arrangements of the thiocyanate ions. When the temperature of the crystal is raised, the reverse arrangement sets in and its fraction increases as the temperature rises; finally the crystal contains an equal number of the normal and reverse arrangements above the transition temperature.

Using the long range order parameter, S, which is defined by the relation: $p=1+S/2$, p being the probability that the thiocyanate ion takes in the normal position, we can now write the intensity of the reflection from the crystal planes $(h\,k\,l)$ whose indices satisfy the relation $h+k+l=2n+1$ in the following form:

$$I(hkl)\propto\{f^{r}-f^{w}\}^{2}S^{2}e^{-2M} \qquad (1)$$

where f^{r} represents the scattering amplitude of the thiocyanate ions in the normal position (the equillibrium position at room temperature), f^{w}, that of the same ion in the reverse position, and the factor e^{-2M}, the reduction factor called the Debye-Waller temperature factor. M can be written in the form:

$$M=8\pi^{2}\langle u^{2}\rangle\left(\frac{\sin\theta}{\lambda}\right)^{2}\equiv B(T)\left(\frac{\sin\theta}{\lambda}\right)^{2} \qquad (2)$$

where $\langle u^{2}\rangle$ is the mean-squared displacement of atoms perpendicular to the reflecting crystal plane.

Therefore, the temperature dependence of S relative to the order parameter, $S(T_0)$, at a certain temperature, T_0, can be given by observed intensities as follows:

$$R(T)\equiv\frac{S(T)}{S(T_0)}=\sqrt{\frac{I(T)}{I(T_0)}}\,e^{-M(T)+M(T_0)} \qquad (3)$$

Throughout this study the room temperature, 15°C, was chosen as T_0. To eliminate the $e^{-M(T)+M(T_0)}$ factor, we proceeded as follows. $M(T)$ for $T=160$°C and $T=15$°C were obtained by examining the observed structure factors $F(h\,k\,l)$ with $h+k+l=2n$, because these reflections are independent of the parameter, S, and the temperature dependence of their intensities mainly comes from the excitation of thermal vibrations. The experimental values of $B(T)$ are 3.1 Å^2 for $T=160$°C and 1.9 Å^2 for $T=15$°C. $M(T)$ at any temperature between $T=160$°C and $T=15$°C was obtained by a linear interpolation. The $e^{-M(T)+M(T_0)}$ factor for the (0 3 2) reflection using these values is 0.931 for $T=142$°C (transition temperature). Therefore, the maximum correction due to thermal vibrations is estimated to be about 7%. As $S(T_0)$ can not be obtained experimentally, it must be given more or less arbitrarily, except that the extrapolation of S to $T=0$°K should tend to unity $[S(0°K)=1]$, corresponding to the completely ordered state.

Discussion

Let us look into the mechanism of the ordering. We shall separate the whole lattice into two body-centered tetragonal lattices and assume that the ordering occurs independently in these two lattices. The interaction energy for one sublattice may then be expressed as:

$$U=-\sum_{i}\sum_{j}J_{ij}\mu_{i}\mu_{j} \qquad (4)$$

where μ_i is the dipole moment of the i'th ionic radical and can take only two values, $\pm\mu_0$, corresponding to the normal and reversed positions. Using the molecular field approximation, we replace μ_i's by an averaged value, $\langle\mu\rangle$, where

$$\langle\mu\rangle=\mu_0\frac{1+S}{2}-\mu_0\frac{1-S}{2}=\mu_0 S \qquad (5)$$

The interaction energy per ion may then be expressed as

$$U=-\mu_0^{2}\sum_{j}J_{0j}S^{2}\equiv -JS^{2} \qquad (6)$$

Following the usual thermodynamical calculations, we obtain the theoretical values of S versus temperatures which are given by the dotted line in Fig. 5. The open circles in the same figure represent experimental values obtained by Eq. 3, assuming $S(T_0)$ to be equal to the theoretical value. However, extrapolation of the experimental curve (solid line) to $T/T_c=0$ does not give $S=1$, which implies

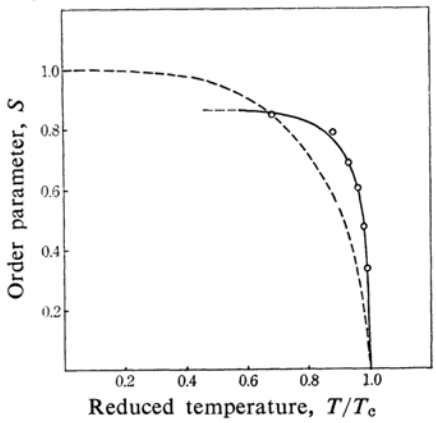

Fig. 5. Temperature dependence of order parameter. Dotted curve is for theoretical value by first approximation. Experimental value is normalized by $S=0.84$.

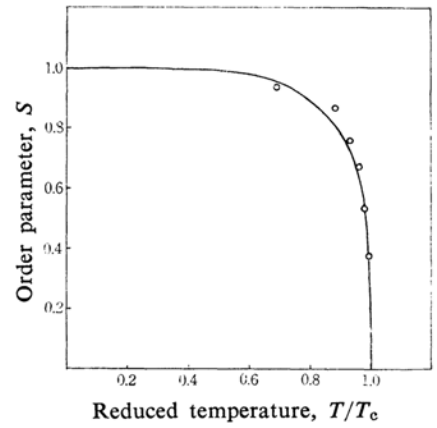

Fig. 6. Temperature dependence of order parameter. Observed values are normalized by $S=0.94$.

that ordering occurs more rapidly in the vicinity of the transition temperature.

As a second approximation, we shall take into account the effect of the volume dependence of the interaction energy, J[4]. If the gain of ordering energy by expansion overcomes the loss of elastic energy, the system will continue to possess the ordering accompanying the anomalous volume expansion near the transition temperature.

A simple calculation along these lines is performed in the Appendix. The results of the calculations give the temperature dependence of S as follows:

$$S=\mathrm{Tanh}\left[\frac{T_c}{T}S+A\frac{T_c}{T}S^3\right]$$
$$A=\frac{2v(\beta_c T_c)^2}{\kappa\alpha^2 k T_c} \qquad (7)$$
$$T_c=2J_0/k$$

where κ is the compressibility; β_c, the anomalous volume expansion coefficient; v, the ionic volume; J_0, the volume-independent part of interaction energy J; k, the Boltzman constant, and α, a parameter given by (A—9), T_c being the Curie temperature. A comparison of the experimental values of the long range order parameter and the values calculated by this equation is given in Fig. 6, where κ is assumed as:

$$\kappa=6.0\times10^{-12}\ \mathrm{cm^2/dyn.}$$

and the following experimental values are used:

$$T_c=142^\circ\mathrm{K}$$
$$\beta_c=4.4\times10^{-4}\ \mathrm{deg^{-1}}$$
$$v=167.5\times10^{-24}\ \mathrm{cm^3}$$

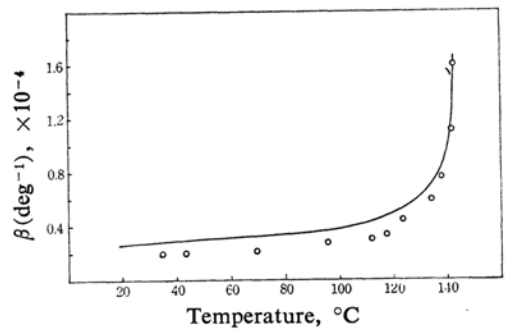

Fig. 7. Temperature dependence of volume expansion coefficient.

For these values,

$$A=0.30$$

As is illustrated in the Appendix, the value of A can not exceed 1/3 for the second order transition, regardless of the value of κ. A comparison of the experimental values of the anomalous volume expansion coefficient β_a and the values calculated by Eq. A—12 is also given in Fig. 7, in which part of the experimental values are given by a dilatation measurement[5].

Substantial accordances in both S and β_a seem to suggest that the transition mechanism is well described by the ordinary molecular field approximation if the volume dependence of the interaction energy is taken into account. The remaining discrepancies may be due to the effect of the excitation of lattice vibrations.

These investigations, however, do not yield any information about the dynamical properties of the flipping motion of the thiocyanate ions.

4) R. Eisenschitz, *Proc. Roy. Soc.*, A 186, 546 (1938).

5) T. Shinoda, H. Suga and S. Seki, This Bulletin, 33, 1314 (1960).

Summary

The phase transition of potassium thiocyanate has been investigated by the X-ray diffraction. It was confirmed that it is an order-disorder type transition with regard to the orientation of the thiocyanate ions. The temperature dependence of the ordering and the anomalous volume expansion near the transition temperature seem capable of being interpreted by the molecular field approximation if the volume dependence of the interaction energy is taken into account.

The authors wish to express their thanks to Professor Syūzō Seki for his kind suggestions for conducting this study. They are also indebted to Miss Takako Shinoda, who, kindly offered the dilatation data, and to Mr. Minoru Sakiyama of Osaka University for his helpful discussions in the course of this work.

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Appendix

The free energy per ion concerning order, including elastic energy, is given by

$$F=\frac{1}{2\kappa}\frac{(\delta v_a)^2}{v}-JS^2+\frac{kT}{2}[(1+S)\ln(1+S)+(1-S)\ln(1-S)] \quad (A-1)$$

where κ is the compressibility, v is the ionic volume and δv_a is the anomalous part of the volume expansion. For small values of δv_a, we have

$$J=J_0+\frac{\partial J}{\partial v}\delta v_a \quad (A-2)$$
$$\equiv J_0+J'\delta v_a$$

The equilibrium volume is determined by the energy minimum condition $\delta F/\delta v=0$, which gives:

$$\frac{\delta v_a}{v}=\kappa J'S^2 \quad (A-3)$$

The substitution of Eq. (A—3) back into (A—1) gives

$$F=-J_0S^2-\frac{\kappa v}{2}J'^2S^4+\frac{kT}{2}[(1+S)\ln(1+S)+(1-S)\ln(1-S)] \quad (A-4)$$

From the equilibrium condition $\delta F/\delta S=0$, the temperature dependence of S is now given by

$$\frac{4J_0}{kT}+S\frac{4\kappa vJ'^2}{kT}S^3=\mathrm{Tanh}^{-1}S$$
$$\cong 2(S+\frac{1}{3}S^3+\cdots\cdots) \quad (A-5)$$

Using the asymptotic form of Tanh S for small S-values, we have an approximate expression for $S(T)$ near the transition temperature as follows:

$$S^2(T)=3\left(\frac{T_c}{T}-1\right)(1-6\kappa vJ'^2)^{-1}$$
$$\equiv\alpha\frac{\Delta T}{T}\approx\alpha\frac{\Delta T}{T_c} \quad (A-6)$$
$$T_c=2J_0k$$
$$\alpha=\frac{3}{1-6\kappa vJ'^2}$$

which means that S^2 depends linearly on the temperature near T_c, the Curie temperature. The unknown parameter, J', is calculated by using the experimental value of the anomalous volume expansion coefficient at T_c as follows:

$$\beta_c=\left[\frac{\mathrm{d}\left(\frac{\delta v_a}{v}\right)}{\mathrm{d}T}\right]_{T=T_c}=\kappa J'\left[\frac{\mathrm{d}S^2}{\mathrm{d}T}\right]_{T=T_c}$$
$$=\kappa J'\frac{\alpha}{T_c} \quad (A-7)$$

Therefore,

$$S^2=3\left(\frac{T_c}{T}-1\right)\left\{1-6\frac{v(\beta_cT_c)^2}{\kappa\alpha^2}\right\}^{-1} \quad (A-8)$$

where α is determined by the self-consistency condition:

$$\alpha=\frac{3}{1-\frac{6v(\beta_cT_c)^2}{\kappa\alpha^2}} \quad (A-9)$$

Finally, we can write the equations to determine S in the form:

$$S=\mathrm{Tanh}\,x \quad (A-10)$$

$$x=\frac{T_c}{T}S+\frac{T_c}{T}AS^3 \quad (A-11)$$

$$A=\frac{2v(\beta_cT_c)}{\kappa\alpha^2}$$

S is obtained by plotting S against x as given by (A—10) and (A—11) and looking for the intercept of the two curves. It should be noticed that S^2 as given by (A—8) is infinite for $A\geqq 1/3$, which implies that the asymptotic expansion of $\mathrm{Tanh}^{-1}S$ up to S^3 is invalid for $A\geqq 1/3$. It can be shown that, in this case, S^2 suddenly becomes zero from a finite value at T_c which corresponds to a first order transition.

Further, the anomalous volume expansion coefficient is calculated by the substitution of $S(T)$ in (A—3) as follows:

$$\beta_a=\frac{\mathrm{d}(\mathrm{d}v_a/v)}{\mathrm{d}T}=\kappa J'\frac{\mathrm{d}(S^2)}{\mathrm{d}T} \quad (A-12)$$
$$=\frac{1}{\alpha}\frac{\mathrm{d}S^2}{\mathrm{d}(T/T_c)}$$