The Phase Transition of Crystalline Potassium Thiocyanate, KSCN. I. Thermal and Infrared Studies

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(Received January 31, 1963)

From the standpoint of the shape of ions, ionic crystals which consist of spherical cations and spherical anions may be the simplest case; there are found almost no materials of this type which undergo phase transition below their melting temperatures. Two exceptions are, however, silver⁽¹⁾ and cuprous⁽²⁾ iodides. In those cases, the transitions are known to be due to the positional disorder of the cations in these crystalline lattices.

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As the second simplest case, ionic crystals which consist of spherical cations and rod-shaped anions may be cited. They are known to undergo a phase transition which may be related to the change in the direction of the anions. Such ionic crystals include, for example, (1) hydrogen, sodium and potassium cyanides³⁾, (2) sodium, rubidium and cesium hydroxides⁴⁾, and (3) sodium, potassium and rubidium hydrosulfides and hydroselenides⁵⁾. The material studied in this paper, potassium thiocyanate crystal, is known to belong to this category.

Another, simpler case may be the ionic crystals which are composed of spherical anions and radical cations. In this case the phase transition due to the orientational or rotational disorder of the cations is well known. Ammonium halides are the most common instances⁶⁾.

Beginning with the view just mentioned, we have studied the phase transition of potassium thiocyanate and ammonium thiocyanate crystals. In the present paper, however, we will confine ourselves to the findings concerning the former.

This crystal is known, by the phase diagram study of Wrzewnewsky⁷⁾, to undergo a phase transition at about 142°C. There have also been some crystallographic and structural chemical investigations by some workers.

The room temperature modification of this crystal has been found to belong to the orthorhombic system by Klug⁸⁾, while infrared studies of this modification by Jones⁹⁾ have shown that the absorption band due to the bending vibration of thiocyanate ions, which should be doubly degenerate, splits into doublets. Plester and Ubbelohde¹⁰⁾ have found in their dilatometric measurements that this substance melts accompanying an anomalously large premelting phenomenon, a phenomenon which they supposed due to the formation of a large number of lattice vacancies. However, our dilatometric study of the extremely purified sample did not show such an anomalous effect¹¹⁾.

It seemed of interest to elucidate the mechanism of the phase transition of this substance on the basis of our knowledge of crystal structure and of the thermal and other properties. For this purpose, we have carried out differential thermal analysis, specific heat measurements from 0 to 165°C, and measurement of the temperature variation of the infrared absorption bands.

Experimental

Materials.—The potassium thiocyanate used for the present studies (extra pure grade reagent of the Wakō Pure Chemicals Co., Ltd.) was recrystallized twice from water and dried at 150°C under a high vacuum (10^{-5} mmHg).

Apparatus and Procedure.—The differential thermal analysis of this substance was carried out by using an automatically controlled recording apparatus, the details of which have already been reported on¹²⁾. In order to determine the transition temperature accurately and in order to study the thermal behavior in more detail, specific heat measurements were also made in the temperature range from 0 to 165°C by using a conduction calorimeter¹³⁾, the heating rate being 0.2~0.3°C/min. A glass-made dilatometer was employed for the measurement of the thermal expansion. The confining liquid used was mercury. It was confirmed that mercury did not react with the sample, even above the melting point¹¹⁾. For the infrared measurements, an Hitachi infrared spectrophotometer EPI-2 with sodium chloride, calcium fluoride and potassium bromide prisms was used. Sample spectra were measured in Nujol mull or epitaxially-grown crystal from melt on a potassium bromide plate. The temperature was varied by an electrical heating device of the sample holder, and the temperature was measured by a copper-constantan thermocouple imposed in a hole drilled in a potassium bromide plate.

Results

Dilatometry.—The general trend of the results has been given in a previous paper¹¹⁾. The detailed behavior around the transition temperature is reproduced here on a large scale in Fig. 1. The curve does not show any of the discontinuity which is usually found in the first order phase transition. The volume thermal expansion coefficients given in Fig. 2 were calculated at each temperature from dilatometric data.

Differential Thermal Analysis.—The results are shown in Fig. 3. Measurements in the temperature range from −190 to 0°C gave no thermal anomaly, so those results are not reproduced here. The anomaly around 140°C is

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5) W. Teichert, *Z. anorg. Chem.*, **247**, 113 (1914).

6) A. W. Lawson, *Phys. Rev.*, **57**, 417 (1940).

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13) I. Nitta, S. Seki, M. Momotani, S. Nakagawa and K. Suzuki, *Proc. Japan Acad.*, **26**, 11 (1950).

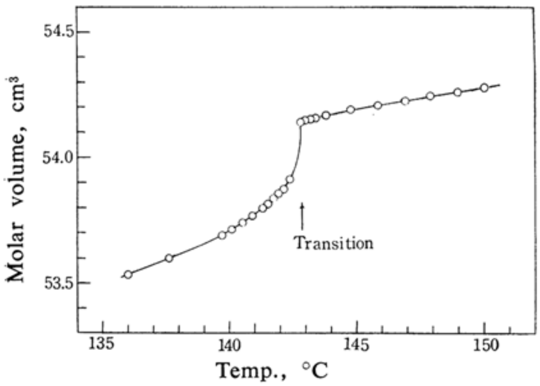


Fig. 1. Temperature variation of molar volume near the transition temperature. (Shinoda, Suga and Seki[11])

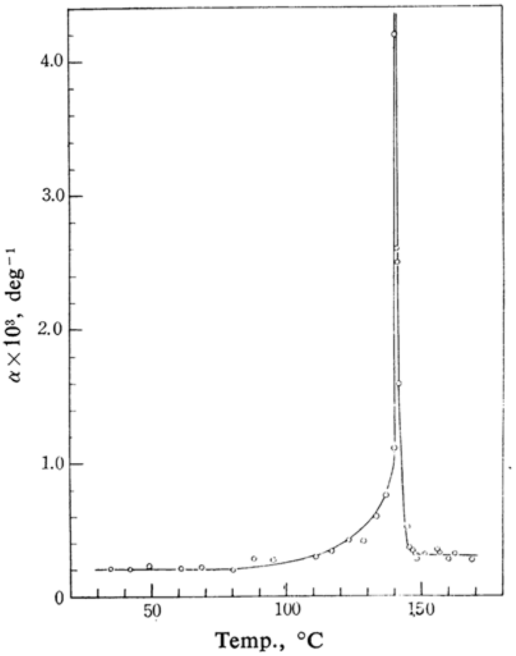


Fig. 2. Volume thermal expansion coefficient vs. temperature curve of potassium thiocyanate crystal.

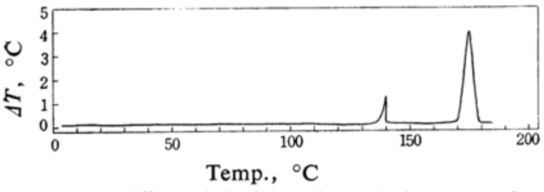


Fig. 3. Differential thermal analysis curve of potassium thiocyanate crystal in the range 0 to 200°C.

due to the phase transition mentioned above, its shape suggesting again that the transition may be of the higher-order type. The higher temperature one at 175°C is ascribed to the melting. As may be seen in the figure, the sharp rise of this curve shows no evidence of the premelting phenomenon suggested by Plester and Ubbelohde[10]. All these results are in good agreement with the results of our dilatometric study[11].

Heat Capacity Measurements.—Heat capacities are tabulated in Table I, while their variation with the temperature is presented in Fig. 4. We can find from this figure that the phase transition is of the so-called "λ-type phase transition", accompanied by a sharp and remarkable rise just below the transition point. No hysteresis phenomenon was observed.

The following thermodynamic quantities were obtained:

Transition temperature: $T_{\mathrm{tr}}=139.2°\mathrm{C}$

Heat of transition: $\Delta H_{\mathrm{tr}}=529.5\pm20$ cal./mol.

Entropy of transition: $\Delta S_{\mathrm{tr}}=1.30\pm0.5$ e. u.

TABLE I. HEAT CAPACITY OF POTASSIUM THIOCYANATE

t, °C	C_{p} cal./deg. mol.	t, °C	C_{p} cal./deg. mol.
8.58	19.97	99.45	28.17
11.15	20.16	101.67	28.45
13.70	20.35	106.10	29.34
17.48	20.47	108.47	29.74
21.23	20.52	111.77	31.23
24.91	20.62	115.03	31.72
28.36	21.07	118.27	32.74
30.84	21.19	120.01	33.52
34.90	21.45	123.09	34.40
37.26	21.70	127.49	38.27
40.49	22.13	130.03	39.93
43.63	22.52	132.53	44.41
45.03	22.58	135.67	53.53
49.87	22.72	136.93	61.03
51.32	22.81	138.18	78.07
53.13	23.20	139.27	560.70
58.50	23.33	139.52	105.23
63.22	23.81	141.08	33.35
67.92	24.09	142.22	31.96
70.72	24.38	144.26	30.72
75.18	24.71	147.33	29.86
78.57	25.07	152.51	29.83
84.92	25.57	156.67	29.85
87.26	25.75	161.92	29.24
90.75	26.31	167.62	30.20
92.97	26.89	169.67	31.43
95.22	27.18		

Infrared Measurements.—The absorption bands are assigned and the notation used is presented in Table II. Our results almost agreed with those by Jones[9] except in one point. We found a complex structure in the strong bands of the 2000 cm⁻¹ region (Fig. 5) which is attributed to the stretching vibration (ν_1) of the C–N bond of SCN⁻ ions, when

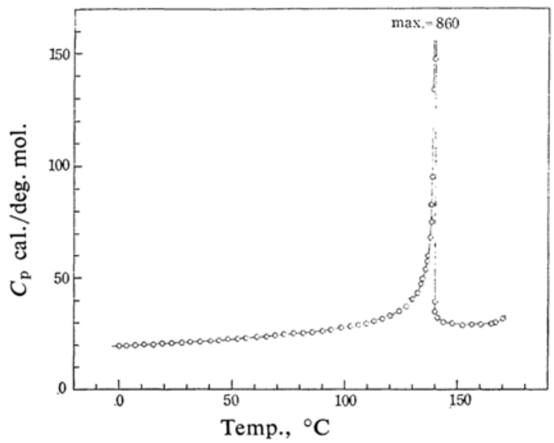


Fig. 4. C_p vs. temperature curve of potassium thiocyanate crystal.

TABLE II. POSITIONS AND ASSIGNMENTS OF INFRARED ABSORPTION BANDS (cm^{-1})

Wave number		Assignment
469	ν_{2b}	Out of plane bending
483	ν_{2a}	In plane bending
745	ν_3	S-C Stretching
944	$2\nu_{2b}=938$	
966	$2\nu_{2a}=966$	
2018		
2040	ν_1	C-N Stretching
2068		

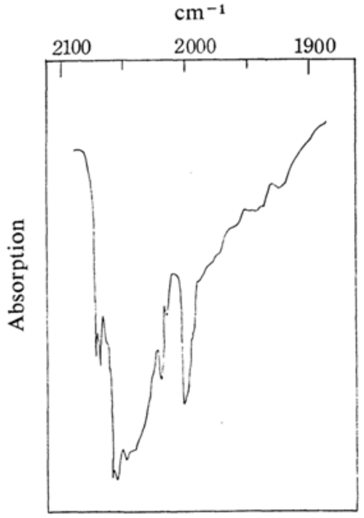


Fig. 5. Infrared spectrum of potassium thiocyanate crystal in the 2000 cm^{-1} region.

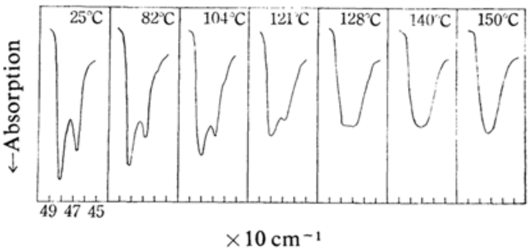


Fig. 6. Temperature variation of ν_{2a} and ν_{2b} bands of SCN$^-$ ion in KSCN crystal.

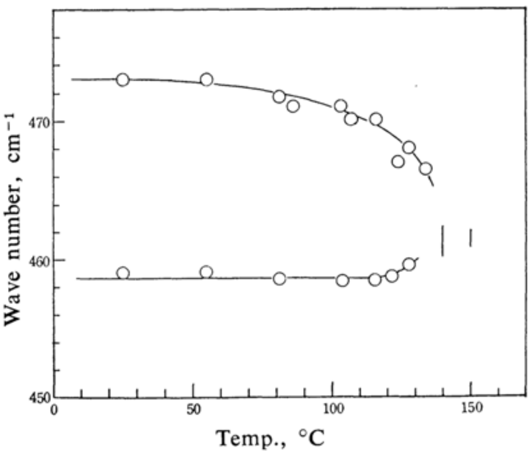


Fig. 7. Temperature dependence of the position of ν_{2a} and ν_{2b} bands of SCN$^-$ ion in potassium thiocyanate crystal.

we measured with a calcium fluoride prism with an epitaxially-grown sample from the melt.

When the sample was heated, gradual changes in the spectrum were observed. The most characteristic change was the apparent transformation of a doublet in the region of 480 cm^{-1} into a singlet. The behavior of and the variation in the positions of these bands are shown in Figs. 6 and 7. We can find that the 483 cm^{-1} band comes closer to the 469 cm^{-1} band as the temperature increases and the variation in wave number difference of these two bands as a function of the temperature accords with the progress of transition shown in molar volume or heat capacity change. Similar behavior was also observed in the position of the ν_3 band. As to the ν_1 band, little variation was found except for the thermal broadening and smearing of its fine structure.

Discussion

The crystal system of phase II (the room temperature phase) is orthorhombic, with $a=6.66$ Å, $b=7.58$ Å, $c=6.635$ Å, $Z=4$, and space group, $D_{2h}^{11}-Pcmb$⁸⁾. The arrangement of ions is schematically given in Fig. 8. The thiocyanate ions lie on a crystallographic b-plane with specified orientations, while potassium ions are sandwiched between the thiocyanate layers.

The molecular symmetry of a "free" thiocyanate ion is $C_{\infty v}$. Three normal modes of vibration, one of which is doubly degenerate,

TABLE III. FACTOR GROUP ANALYSIS OF KSCN CRYSTAL IN PHASE II

$p=16,\ s=8,\ v=4,\ s\text{-}v=4$

D_{2h}^{11}		Screw				Axial glide		Axial glide	N	T	T'	R'	n	IR	Raman
	E	C_2^c	C_2^b	C_2^a	i	σ_c	σ_b=m	σ_a							
A_{1g}	1	1	1	1	1	1	1	1	7	0	3	1	3	—	$\alpha_{aa}, \alpha_{bb}, \alpha_{cc}$
A_{1u}	1	1	1	1	−1	−1	−1	−1	4	0	2	2	0	—	—
B_{1g}	1	−1	1	−1	1	−1	1	−1	8	0	4	1	3	—	α_{ca}
B_{1u}	1	−1	1	−1	−1	1	−1	1	5	1	2	2	0	M_b	—
B_{2g}	1	1	−1	−1	1	1	−1	−1	5	0	3	2	0	—	α_{ab}
B_{2u}	1	1	−1	−1	−1	−1	1	1	8	1	3	1	3	M_c	—
B_{3g}	1	−1	−1	1	1	−1	−1	1	4	0	2	2	0	—	α_{bc}
B_{3u}	1	−1	−1	1	−1	1	1	−1	7	1	2	1	3	M_a	—
$U_R(p)$	16	0	0	4	0	0	12	0	↑	↑	↑	↑			
$U_R(s)$	8	0	0	4	0	0	4	0							
$U_R(s\text{-}v)$	4	0	0	0	0	0	4	0							
$\pm1+2\cos\phi_R$	3	−1	−1	−1	−3	1	1	1							
$\chi'_R(N)$	48	0	0	−4	0	0	12	0							
$\chi'_R(T)$	3	−1	−1	−1	−3	1	1	1							
$\chi'_R(T')$	21	1	1	−3	3	−1	3	−1							
$1\pm2\cos\phi_R$	3	−1	−1	−1	3	−1	−1	−1							
$\chi'_R(R')$	12	0	0	0	0	0	−4	0							

p, s and v: Total number of atoms, ions and polyatomic ions in a Bravais unit lattice, respectively.

ϕ_R: Angle of rotation in the operation R.

$U_R(p)$, $U_R(s)$ and $U_R(s\text{-}v)$: Total number of atoms, ions and polyatomic ions the centers of gravity of which are invariant under the operation R, respectively.

$\chi'_R(N)$, $\chi'_R(T)$, $\chi'_R(T')$ and $\chi'_R(R')$: Characters of representation based on the coordinates of all the degrees of freedom of motion in a Bravais unit lattice, mere translation of the whole of a Bravais unit lattice, translational lattice vibrations of ions, and rotational lattice vibrations, respectively.

N: Total number of degrees of freedom of motion in a Bravais unit lattice.

T, T', R' and n: Numbers of degrees of freedom of translation, translational lattice vibration, rotational lattice vibration and inner vibration of ions in a Bravais unit lattice, respectively.

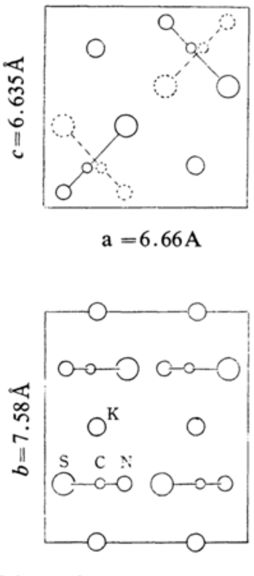


Fig. 8. Schematic representation of the unit cell of potassium thiocyanate crystal.

are those shown in Fig. 9. From the standpoint of site symmetry analysis, Jones[9] explained the splitting of the ν_2 band into a doublet in the crystalline state as the result of the anisotropy of the crystalline field that is brought about by the layer structure of crystal. The absorption bands at 483 and 469 cm^{-1} were assigned on the basis of the polarisation studies to the bending vibrations parallel with (ν_{2a}) and perpendicular to (ν_{2b}) the crystallographic b-plane respectively.

In the present study, a remarkable temperature shift of position was observed to take place in the ν_{2a} and ν_3 bands, both due to a in-plane vibration, while no such tendency was found in the ν_{2b} (out-of-plane) band. These experimental results suggest that phase transition takes place in such a way that the crystalline field parallel with the b-plane around a thiocyanate ion is much influenced in the course of phase transition. As is shown in Fig. 10, the thiocyanate ions in the b-plane are arranged in the closest packing way, so the overlapping of an electron cloud between atoms

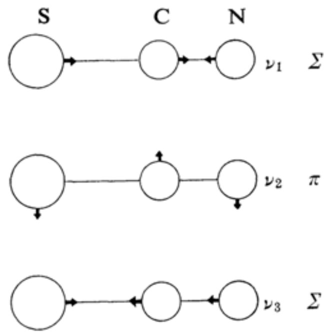


Fig. 9. Schematic representation of normal modes of vibration of SCN$^-$ ion.

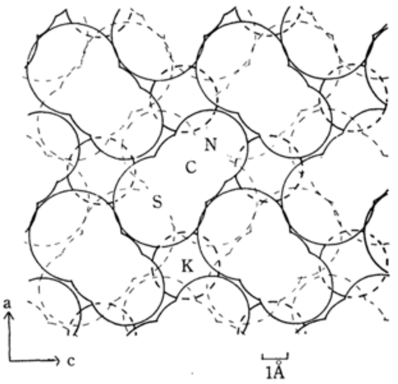


Fig. 10. Schematic representation of the packing of ions projected to b-plane. (phase II).

in the plane is more profound than that between the inter-layer atoms. The above-mentioned remarkable change in the ν_{2a} and ν_3 bands may be understandable by means of this line of explanation.

Now, we should like to proceed to the problem of the thermal properties of the crystal before entering into a discussion of the relationship between the spectroscopic results and the mechanism of phase transition. The molar volume and the thermal expansion coefficient versus the temperature curves reveal that this transition is of a higher order (see Figs. 1 and 2). This means that the crystal structure of the high temperature phase is nearly the same as the low temperature one, with no appreciable change in atomic arrangement. It is also found from the C_p vs. temperature curve that the transition is highly co-operative, as is evident from the sharp rise just below the peak. The amount of transition entropy, 1.30±0.05 e. u., is nearly equal to $R \ln 2 = 1.38$ e. u. Combining these results of transition entropy and of dilatometry, it is strongly suggested that phase I maintains nearly the same arrangement of the centers of gravity of ions and obtains two opposite directions (S–C–N and N–C–S) in one and the same orientation (original to phase II) of anions in equal probability.

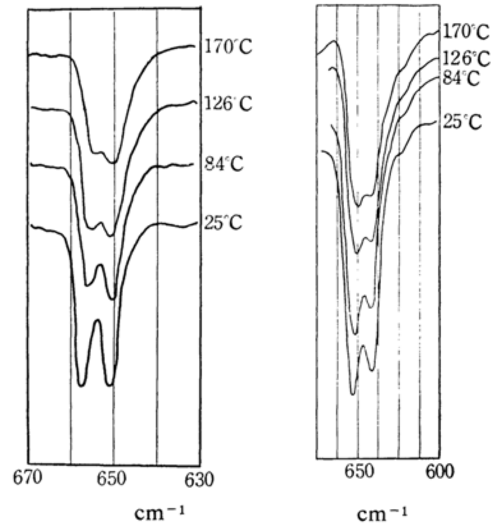
Recently, X-ray crystal structure analysis of phase I (the high temperature phase) has been carried out by Yamada and Watanabé[14], who found that the crystal in phase I belongs to the tetragonal system (space group, D_{4h}^{18}–I4/mcm, $Z=4$) and that the electron distribution map of a thiocyanate ion does not differentiate S and C atoms. This means that an averaged structure between two equilibrium directions (S–C–N and N–C–S) in one and the same orientation is obtained. These results are in good agreement with our results.

From these facts, we can conclude that the transition is of the order—disorder type for two directions of thiocyanate ions.

Next, we should like to discuss our spectroscopic results in connection with the mechanism of the phase transition.

As is shown in Figs. 2, 4 and 7, the volume thermal expansion coefficient, the molar heat capacity and the wave number of the infrared ν_{2a} band all start to change at nearly the same temperature, 70°C. These facts show that the temperature shift of the ν_{2a} frequency is intimately related to the progress of the phase transition.

As has been mentioned, the crystal in phase I belongs to the tetragonal system, but the layer structure of the thiocyanate ions is still maintained. Therefore, if the splitting of the ν_2 band observed in phase II is ascribed to the anisotropy of the crystalline field around a



(a) KN$_3$ (b) KNCO

Fig. 11. Temperature variation of infrared ν_2 bands of KN$_3$ and KNCO crystals.

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[14] Y. Yamada and T. Watanabé, This Bulletin, 36, 1032 (1963).

thiocyanate ion, a similar ascription should hold also in phase I.

In this respect, we have taken infrared spectra of potassium azide, KN_3 and potassium cyanate, KNCO, crystals for reference. These crystals consist of linear triatomic anions and potassium cations and are quite isomorphous with potassium thiocyanate crystal in phase I (space group, $D_{4h}^{18}-I4/mcm$)[15,16]. In these two crystals the size of anions is the smaller and they are packed more closely, as is reflected in the lattice constants ($a=c=6.096$ Å, $b=7.056$ Å for KN_3 crystal; $a=c=6.07$ Å, $b=7.03$ Å for KNCO crystal), and the thermal motions mainly responsible for the reorientation occur with more difficulty because of their stronger interionic interactions, as is revealed by their higher melting points (355°C for KN_3 and ca. 700°C for KNCO). Spectra of these compounds in the ν_2 region at various temperatures above room temperature are presented in Fig. 11. As is evident from the figure, splitting may be observed at all the temperatures examined, accompanied by a slight shift of higher frequency bands*. From these facts, it is very plausible to assume that we can ascribe the transformation of a doublet into a singlet observed in the ν_2 band of the potassium thiocyanate crystal, not to the fact that this crystal belongs to the tetragonal crystal system in phase I, but rather to an excitation of violent torsional oscillation as well as to a flipping motion which leads to the dynamical directional disordering of the thiocyanate ions.

Inspection of the molecular packing in the potassium thiocyanate crystal of phase II (Fig. 10) shows that out-of-plane motions seem to occur more easily than in-plane motions. Furthermore, from X-ray studies by Yamada and Watanabé[14] it has been established that the expansion of the b axis of a unit cell at the end-point of phase transition is more remarkable than those along the a and c axes ($\Delta b/b \simeq 0.017$, $\Delta a/a \doteqdot \Delta c/c \simeq 0.008$). This fact is considered to reflect also the fact that interionic interactions along b-axis are weaker than those along the other two axes, so out-of-plane motions will be more frequently excited than in-plane motions. Although the torsional frequencies of thiocyanate ions are not known, the existence of a lattice frequency of 28 cm^{-1} has been reported by Jones[8]. In any case, it is quite plausible that torsional frequencies are of the order of one-tenth of the bending frequencies. The period of flipping motions from one equilibrium direction to another will be larger than or at least of the same order as those of the torsional oscillation. Therefore, in one period of torsional oscillation some ten cycles or so of bending vibration are possible. Such out-of-plane motions will diminish the repulsive potential, which affects in-plane bending vibration more seriously. Frequent excitation of such kinds of motion all over the crystal will work out to bring about operatively a considerable decrease in the crystalline field around the anions.

Summarizing these results, we may explain the temperature variation of the ν_{2a} band in the following way. When the temperature approaches the transition temperature, the out-of-plane torsional oscillation and the flipping motion of thiocyanate ions are more and more frequently excited; eventually, at the transition point the long-range directional order of thiocyanate ions will disappear completely. Parallel with the progress of the phase transition, the repulsive potential, as well as the anisotropy mentioned above, will be gradually decreased, resulting in the gradual shift of the ν_{2a} band.

Finally, we should like to comment briefly on the results of the factor group analysis of the molecular vibrations of thiocyanate ions in the potassium thiocyanate crystal (phase II). In this case a Bravais unit lattice coincides with a crystallographic unit cell, and there are four potassium cations and four thiocyanate anions in a unit cell. The analysis was performed following the ordinary method; the results are presented in Table III. If a thiocyanate ion is linear, $4\times(3\times3-5)=16$ inner vibrational modes will be present. Nevertheless, only twelve modes are found by this analysis. On the other hand, twelve modes are found for the rotational lattice vibration. If thiocyanate ions are strictly linear, there should be present only $4\times2=8$ rotational vibrational modes in a Bravais unit lattice. Thiocyanate ions are thus found by this analysis to be not strictly linear-shaped but slightly bending, even in the equilibrium configuration, under the influence of the intermolecular interaction. Of the twelve rotational lattice modes, four are out-of-plane modes, distributed among the A_{1u}, B_{1u}, B_{2g} and B_{3g} species. The out-of-plane bending vibration in the nomenclature of the site symmetry analysis corresponds to the rotational lattice modes which fall in B_{1u}.

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[15] S. B. Hendricks and L. Pauling, *J. Am. Chem. Soc.* **47**, 2904 (1925).

[16] L. K. Frevel, *Z. Krist.*, **94**, 197 (1936); *J. Am. Chem. Soc.*, **58**, 779 (1936).

* Infrared spectra of these two crystals have been reported by some authors. For KN_3, see P. Gray and T. C. Waddington, *Trans. Faraday Soc.*, **53**, 901 (1957); H. A. Papazian, *J. Chem. Phys.*, **34**, 1614 (1961). For KNCO, see T. C. Waddington, *J. Chem. Soc.*, **1959**, 2499. These writers have, however, not made any comment regarding on the splitting of the ν_2 band nor have they presented a spectrum chart in which no doublet is observed. We should like to make a more detailed discussion of this point elsewhere in the near future.

As has been mentioned above, in phase I the direction of the thiocyanate ions is disordered. Since the space group of this phase represents the symmetry of the averaged structure, factor group analysis cannot be successfully applied to this phase. However, phase I belongs to the tetragonal system, and at least no positive reasons are available which oblige us to consider that thiocyanate ions bend in this phase. If so, the temperature shift of the ν_{2a} band may be accompanied by the change in molecular shape from slightly bending to strictly linear in the equilibrium configuration, but by no change in the mode of molecular motion. On the other hand, in the bending vibration which falls in the B_{3u} species, a change in the shape of the ions as well as a change in the mode of motion (from a rotational lattice one to a bending one) may be expected to occur, but no appreciable shift in the ν_{2b} frequency is observed.

Summary

The phase transition of the potassium thiocyanate crystal at ca. 140°C has been studied by thermal and infrared methods. The transition is of a higher-order type, accompanied by an entropy change of 1.30 ± 0.05 e. u., which is nearly equal to $R\ln 2$. The infrared band due to the in-plane bending vibration of a thiocyanate ion shifts to lower frequencies in the course of the phase transition. From these results, it has been concluded that the phase transition is connected with the dynamical disordering of the direction of thiocyanate ions in crystal, a disordering which is mainly brought about by the frequent excitation of the out-of-plane torsional oscillation and the flipping motion.

We wish to express our hearty thanks to Professor Isamu Nitta of Kwansei Gakuin University for his valuable advice and continued interest in this study, and also to Drs. Yasusada Yamada and Tatsuo Miyazawa of Osaka University for their kind discussions. This work was partly supported by Scientific Research Funds from the Ministry of Education.

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