

21-Crystallography at Non-Ambient Temperatures and/or Pressures; Phase Transitions

foil attenuators as reported in PF Acta Rept. #7 (1989) 177. Fig 1 shows Laue spots of solid ^3He taken by use of white X-rays. The texture of solid ^3He changes with annealing time, which could not be observed in solid ^4He . Fig. 2 shows the Laue spots (422, 844) of Ho-elpasolite taken at 830mK, 65mK and 320mK by white X-rays and is more suitable for diffractometry than for topography from its characteristics. A structural phase transformation at 150mK predicted from other experiments was confirmed from splitting of a Laue spot as a change of atomic arrangement within unit cell as seen in Fig. 2.

Fig. 1 The topographs of solid ^3He in serial order (a)920705-22:25, (b)920705-23:15 and (c)920706-08:49.

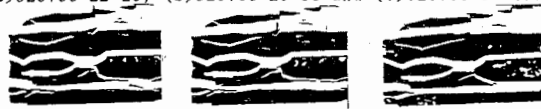


Fig. 2 The temperature change of Laue spots of $\text{Cs}_2\text{NaHoCl}_6$ at (a)830mK, (b)65mK and (c)320mK.



MS-21.02.07 STRUCTURE OF LOW TEMPERATURE PHASE OF ISOLATED HYDROGEN BOND SYSTEM $\text{K}_3\text{D}(\text{SO}_4)_2$. By Y. Noda*, H. Kasatani*, I. Tamura, Y. Kuroiwa and H. Terauchi*, Faculty of Science, Chiba University, Yayoi, Chiba 263, Japan, *School of Science, Kwansai Gakuin University, Uegahara, Nishinomiya 662 Japan.

The pair $\text{K}_3\text{D}(\text{SO}_4)_2$ and $\text{K}_3\text{H}(\text{SO}_4)_2$ is a textbook example of an extraordinary isotope effect for phase transition temperatures. The D-compound has a finite T_c at 84K while the H-compound has no phase transition. The structures feature two SO_4 groups connected by one hydrogen atom forming an isolated dimer. The high temperature phases of H and D compounds are isostructural with virtually identical atomic parameters. The structure analyses of the H-compound in the A2/a phase at various temperatures down to 27K were already performed. (Y. Noda, H. Kasatani, Y. Watanabe and H. Terauchi, J. Phys. Soc. Jpn., 1992, 61, 905-915): Several Bragg reflections violating the A-lattice centering were observed below T_c in the D-compound (Y. Noda, Y. Watanabe, H. Kasatani, H. Terauchi and K. Gesi, J. Phys. Soc. Jpn., 1991, 60, 1972-1977). The structure analysis of the low temperature phase of the D-compound described here was accordingly performed in space group $\text{P2}_1/\text{a}$. A Weissenberg photograph is presently being exposed at 12K, using a new technique with an image plate, to establish firmly the space group. Observed hydrogen bond length $R_{\text{O}\cdot\text{O}}(\text{D})$ is shown in Fig.1 as a function of temperature, above and below T_c . In the figure, the temperature dependence of $R_{\text{O}\cdot\text{O}}(\text{H})$ is also shown, which does not show any anomaly as a function of temperature. The low temperature phase seems to be characterized by an antiparallel ordering of hydrogen atoms.

The image plate study is supported by The Mitsubishi Foundation.

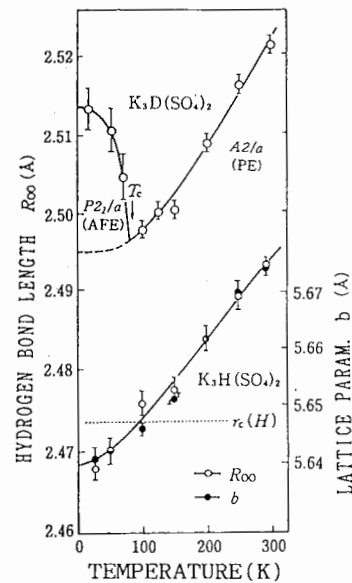


Fig.1. Temperature dependence of hydrogen-bond lengths

PS-21.02.08 CRYSTAL STRUCTURE OF K_2SO_4 AT 15 K.

By K. Ojima*, Y. Nishihata, and A. Sawada, Faculty of Science, Okayama University, Japan.

Crystal structure analyses at very low temperatures are fundamental for clarifying solid state properties such as superconductivity, ferroelectricity and magnetism. But there have not been so many reports because of instrumental difficulties. Recently we have set up a new diffractometer which can be easily used in a routine work to make crystal structure analyses at very low temperatures down to 10K; a four-circle automatic diffractometer with an offset χ -circle of inner diameter 400 mm (Huber Eulerian cradle model 512). The low-temperature device is a closed-cycle He-gas refrigerator (Cryomech GB15) which is mounted on the ϕ -circle of the four-circle diffractometer. This small and light refrigerator enables us to maintain the sample shift within $10\mu\text{m}$ from the center of the χ -circle during data collections. We can measure Bragg reflections in a wide range of χ -circle ($-90^\circ \leq \chi \leq 90^\circ$).

The crystal structure of K_2SO_4 at room temperature was reported by McGinnety(1972). It was suggested that K_2SO_4 crystal might undergo a phase transition at 56 K from measurements of specific heat and dielectric constant (Gesi, Tominaga & Urabe, 1982). The purpose of the present work is to examine the crystal structure of K_2SO_4 at 15 K and to examine whether such phase transition really occurs or not. The crystal structure was studied at both 296 and 15 K. Intensity data were collected up to $(\sin/\lambda)_{\text{max}}=0.904 \text{ \AA}^{-1}$. The structure was refined by a block-diagonal-matrix least-squares on F, using the program AXS-89 system which were rewritten from UNICS by Mashiyama(1991). The crystal at 296 K was confirmed to be orthorhombic, Pmcn, with $Z=4$. The calculation converged at $R=0.045$, $wR=0.043$ for 1281 independent reflections with $F \geq 3\sigma(F)$. The crystal at 15 K was found to be orthorhombic, Pmcn, with $Z=4$. The calculation converged at $R=0.037$, $wR=0.034$ for 1375 independent reflections with $F \geq 3\sigma(F)$. Isotropic thermal parameters U_{eq} of K and O atoms at 15 K reduce to

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about one sixth of those at 296 K, and that of S atom reduces to one tenth (Table 1).

Table 1. Unit cell parameters and atomic positions of K_2SO_4 at 15 K and 296 K

Unit cell parameters at 15 K				
	a (Å)	b (Å)	c (Å)	
	5.7226(4)	9.9985(4)	7.4218(3)	
Atomic position at 15 K				
atom	x	y	z	U_{eq} (Å ²)
K1	0.25	0.58951(5)	0.67139(6)	0.00258(8)
K2	0.25	0.29720(5)	-0.01118(9)	0.00218(8)
S	0.25	0.57985(5)	0.23261(7)	0.00086(10)
O1	0.25	0.5828(2)	0.0344(2)	0.0047(3)
O2	0.25	0.4399(2)	0.2939(2)	0.0037(3)
O3	0.0390(2)	0.6486(1)	0.3015(2)	0.0038(2)
	R=0.037	wR=0.034		
Unit cell parameters at 296 K				
	a (Å)	b (Å)	c (Å)	
	5.7704(3)	10.0712(9)	7.4776(4)	
Atomic position at 296 K				
atom	x	y	z	U_{eq} (Å ²)
K1	0.25	0.58936(7)	0.6742(1)	0.0161(1)
K2	0.25	0.29544(7)	-0.01082(9)	0.0138(1)
S	0.25	0.58006(7)	0.23300(9)	0.0082(1)
O1	0.25	0.5829(3)	0.03719(3)	0.0251(7)
O2	0.25	0.4426(2)	0.2970(3)	0.0188(6)
O3	0.0421(3)	0.6480(2)	0.3005(2)	0.0199(4)
	R=0.045	wR=0.043		

McGinney, A. (1972). *Acta Cryst.* B28, 2845.

Gesi, K. Tominaga, Y. & Urabe, H. (1982). *Ferroelectrics.* 44, 71.

Mashiyama, H. (1991). *J. Phys. Soc. Jpn.* 60, 180.

PS-21.02.09 TIME-RESOLVED X-RAY POWDER DIFFRACTION STUDY OF POLYMORPHISM IN COBALT NITRATE HEXAHYDRATE AND PHASE TRANSFORMATIONS AT LOW TEMPERATURES. By J. Plevert*, H. Hashizume and D. Louer¹, Tokyo Institute of Technology, Japan, ¹University of Rennes, France.

Three polymorphs of $Co(NO_3)_2 \cdot 6H_2O$ are known to exist at low temperatures. When the room-temperature phase is cooled at high cooling rates, the low-temperature phase is produced by a burst effect in the crystal during the martensitic transformation. For slow cooling rates, an intermediate phase is obtained (P. Pouillen & al. (1965). *C. R. Acad. Sc. Paris*, 260, 6861). Moreover the hygroscopic properties of the sample are an important factor of the phase stability. The modification of environmental conditions brings a new phase.

Powder patterns recorded at low temperatures using a position sensitive detector provide information about the kinetics of the martensitic transformation. The structural information of different phases obtained from these data provides the relationship between the polymorphs, and allows the driving force of the phase change to be determined.

21.03 – Phase Transitions in Crystals

MS-21.03.01 The Landau-free-Energy expansion for the phase transition in liquid crystals

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The theoretical investigation of the phase transition between the different liquid crystal smectic phases is performed after applying the Landau approach. The descriptions of the free energy are given according to the Landau-Lifshitz condition. The X-ray flat patterns during the phase transition are discussed.

The analysis shows a wide variety of the symmetry allowed phase transitions in ordered smectics. The results for the space symmetry group are presented. Beside this, some experimentally detected smectic phases, e.g. the hexatic smectic (D_{6h}), smectic F and I (C_{2h}), unstuck smectic B (D_{6h}^1), smectic E (D_{2h}^9), smectic J and G (C_{2h}^3), smectic H and K (C_{2h}^5), are discussed especially.

As the first step here, only the transitions with change of space group are presented. It should be pointed out that some transitions may lead to the phases with the same symmetry group and another unit cell.

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MS-21.03.02

A SOLID-SOLUTION THEORY OF ANESTHETIC INTERACTION WITH MEMBRANES, By Y. Suezaki, Physics Laboratory Saga Medical School, Saga 849, Japan.

Anesthetics (or any other small molecules) depress the temperature of the main phase transition of phospholipid bilayers. Certain anesthetics widen the temperature span of the transition, whereas others do not. The widening in the first-order phase transition is intriguing.

In this report, the effect of additive molecules on the transition temperature and its temperature span were explained by the solid-solution theory. By assuming the coexistence of the liquid-crystal and solid-gel phases of lipid membranes at phase transition, the phase boundary is determined from the distribution of anesthetic molecules between the liquid-crystal membrane versus water and the solid-gel membrane versus water.

The theory shows that when the lipid concentration is large or when the lipid solubility of the drug is large, the temperature width of the transition increases, and vice versa. Highly lipid-soluble molecules such as long-chain alcohols and volatile anesthetics, increase the temperature width of the phase transition when the lipid:water ratio is large, whereas highly water-soluble molecules, such as methanol and ethanol, do not. The aqueous phase serves as the reservoir for anesthetics. Depletion of the additive molecules from the aqueous phase is the cause of the widening. When the reservoir capacity is large, the temperature width does not increase. The theory also predicts asymmetry of the specific heat profile at the transition. (Y. Suezaki, T. Tatara, Y. Kaminoh, H. Kamaya and I. Ueda, *Biochim. Biophys. Acta*, 1990, 1029, 143. and Y. Suezaki, H. Kamaya and I. Ueda, *Phase Transitions*, 1990, 29, 37.)