

## 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  $^3\text{He}$  taken by use of white X-rays. The texture of solid  $^3\text{He}$  changes with annealing time, which could not be observed in solid  $^4\text{He}$ . 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  $^3\text{He}$  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  $\text{SO}_4$  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.

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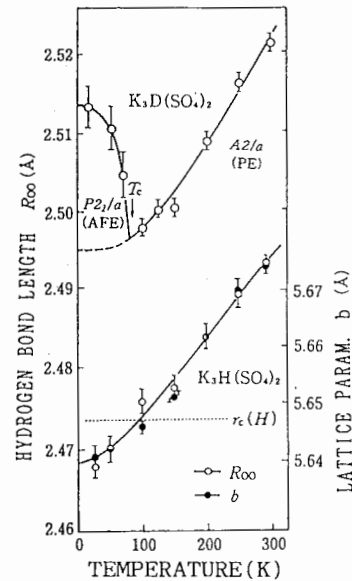


Fig.1. Temperature dependence of hydrogen-bond lengths

PS-21.02.08 CRYSTAL STRUCTURE OF  $\text{K}_2\text{SO}_4$  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  $\chi$ -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  $\phi$ -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  $\chi$ -circle during data collections. We can measure Bragg reflections in a wide range of  $\chi$ -circle ( $-90^\circ \leq \chi \leq 90^\circ$ ).

The crystal structure of  $\text{K}_2\text{SO}_4$  at room temperature was reported by McGinnety(1972). It was suggested that  $\text{K}_2\text{SO}_4$  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  $\text{K}_2\text{SO}_4$  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