

07.2-08 THE STRUCTURAL CHANGES IN THE EDGE OF THE CRYSTAL AT HIGH TEMPERATURE. By R. Łappa, Dept. of Physics, Agricultural and Teachers University, Siedlce, Poland.

The mechanism of structural changes in the edge of the crystal at high temperature is treated on the ground of theoretical and experimental data concerning surface properties of the solid. It is shown that theoretically predicted non-equilibrium excess of vacancies in surface region of the crystal gives rise to condensation of vacancies into microvoids. These latter cause strong mechanical stresses in the crystal lattice and result in generation of dislocations and even slip bands. In the work concerning X-ray topographic investigation of dislocation-free Si monocrystal at melting temperature (J.I. Chikawa, *J. Cryst. Growth*, 24/25 (1974) 65) it is shown that the described effects really exist and thus support the thesis about the dominating role of surface phenomena in the melting process of the solid. The paper also deals with statistical model of described order-disorder transition in surface layers of the crystal and on this basis some thermodynamical parameters of the analysed system are calculated.

07.3-01 A DISTRIBUTION OF CATIONS IN α -AgI TYPE SUPERIONIC CONDUCTORS. By S. Hoshino, H. Fujishita and T. Sakuma*, Institute for Solid State Physics, the University of Tokyo, Tokyo and *Faculty of Science, Ibaraki University, Mito, Japan.

The neutron diffuse scattering of α -AgI type superionic conductors. α -AgI, α -Ag₂S and α -Ag₃SI was measured using either powder samples or single crystals with a triple-axis type neutron spectrometer. The purpose of this experiment was to examine a static state of order in the distribution of cations by the method of a separation of elastic disorder scattering from inelastic thermal scattering. The analyzer crystal was mounted at a fixed angle so as to measure only elastic part of the scattering though a part of quasi-elastic scattering was included due to the experimental energy resolution.

The experimental diffuse scattering intensity was compared with calculated ones with various models. A good agreement between experiment and calculation has been obtained when we took account of the structure model of a twelve position distribution with asymmetric anharmonic thermal vibration (S. Hoshino et al. (1977), *Solid State Commun.* 22, 763. and R.J. Cava et al. (1977), *Solid State Commun.* 24, 411.) with an appropriate short range order among cations in these positions. The unit cell of bcc lattice of α -AgI, α -Ag₃SI and α -Ag₂S contains, on the average, two, three and four Ag atoms, respectively. Therefore, a degree of interaction among cations should be somewhat different in these three crystals. This causes a difference in the short range order parameter.

Referring to various X-ray and neutron scattering studies especially to a "liquid-like" structural model, the distribution and the diffusion mechanism of cations in the α -AgI type superionic conductors are discussed.

07.3-02 ⁷Li NMR INVESTIGATIONS IN IONIC CONDUCTOR LiC₂ OR LiI CONTAINING DSPP. By Wang Gang, Li Zhirong, Chen Li-quan and Zhao Zong-yuan, Institute of Physics, Academia Sinica, Beijing, China.

In order to understand the mechanism of the ionic conductivity enhancement in the system of LiC₂ (or LiI) containing dispersed second-phase particles (DSPP), we have performed ⁷Li NMR investigations of both line width and spin-lattice relaxation time (T_1) at 35 MHz in the temperature range of 173 - 483°K. An additional peak was observed to overlap the resonance absorption line. The signal-to-noise ratio was obviously increased while T_1 decreased. The profile of this peak changes with both type and content of DSPP and with temperature. It is concluded that the ionic conductivity enhancement and the appearance of the additional peak are both caused by the DSPP (submicron size). The high conduction in the space charge region near the interface between LiC₂ or LiI and DSPP is suggested as a possible mechanism for the ionic conductivity enhancement and the appearance of the additional peak.

07.3-03 THE ABNORMAL SCATTERING OF LIGHT IN AN α -LITHIUM IODATE SINGLE CRYSTAL UNDER THE ACTION OF A DC FIELD. By Yang Hua-guang, Xu Zheng-yi, Li Chen-xi, Zhang An-dung, Xu Gang and Li Yin-yuan, Institute of Physics, Chinese Academy of Sciences, Beijing, China.

When a laser beam passes through an α -lithium iodate single crystal under the action of a dc field along the c-axis, it is found that bands of scattered light ring around the crystal are produced. The scattering directions of the light are almost perpendicular to the c-axis if the incident beam is perpendicular to that axis. When the electric vector of the incident beam is perpendicular to the c-axis, then that of the scattered beam would be parallel to the c-axis; when the former is parallel to the c-axis, then the latter would be perpendicular to the c-axis. If the former is neither perpendicular nor parallel to the c-axis then two bands would appear, the electric vectors of which are parallel and perpendicular to the c-axis, respectively. Under specific conditions, these bands coincide. We called it abnormal scattering of light (Yang Hua-guang, *Acta Physica Sinica* (1980), 29, 1039). No frequency shift between the scattered and incident beam larger than 15 MHz has been observed. The distribution of intensity of the band is asymmetric with respect to the transmitted light spot; one side is stronger than the other. We have found that the distributions of intensity of the scattering band are inverse for the two types of absolute configuration of α -lithium iodate single crystals; that is, the stronger side of the band for the D type crystal corresponds to the weaker side for the L type crystal. The relationship between location of bands and that of the transmitted light spots is dependent on the orientations of the incident and exit surfaces of specimen with respect to the c-axis of the crystal. The intensity of scattering of light depends on the current in the crystal. The fine structure of these bands and the

relaxation behaviour of the scattering phenomenon have been studied in detail.

α -lithium iodate is a quasi 1-dimensional ionic conductor whose carriers are interstitial Li ions and Li vacancies (Zhang An-dung *et al.*, Acta Physica Sinica (1980) 29, 1158). The local deformation of the crystal takes place when the carriers are migrating under the action of a dc field. The fluctuations of the strain in the crystal cause fluctuations of the optical axis. The thermal average values of the dielectric tensor element ϵ_{xz} and ϵ_{yz} are non-zero and have spatially periodic distribution (caused by defects). Therefore, the abnormal scattering of light will be produced (P. G. de Gennes, The Physics of Liquid Crystals, sec. 3.4).

oxygen in the spinel-block and the occupation of the crystallographic site varies from 0.17 at low temperature to 0.10 at 620K.

Other hydrogens are strongly delocalized in the conduction region, forming long (O-H)-lengths (1.73 Å); no definite evidence of the existence of an H_3O^+ entity has been found during this structural study. At the higher temperature, there are less hydrogen atoms and their thermal vibration amplitudes are large, so that it becomes more difficult to locate them precisely. However, some of these hydrogens seem to be distributed around the oxygen which links the spinel-blocks together.

These results emphasize the possibility that the delocalized hydrogens participate in the conduction mechanism.

07.3-04 TEMPERATURE DEPENDENCE OF THE HYDRATED HYDROGEN β'' -ALUMINA STRUCTURE BY NEUTRON DIFFRACTION STUDY. By M. Anne and D. Tranqui, Laboratoire de Cristallographie, C.N.R.S., 166X, 38042 Grenoble Cedex, France, and W. L. Roth, General Electric Research and Development Center, P.O. Box 8, Schenectady, NY 12301 U.S.A., and M. S. Lehmann, I.L.L., 156X, 38042 Grenoble Cedex, France.

Following previous conductivity measurements, quasielastic neutron scattering and thermal gravimetric analysis on hydrated hydrogen β'' -alumina, a neutron diffraction study on a single crystal has been undertaken. The interesting physical properties of this compound called for a precise structure analysis. Hydrated hydrogen β'' -alumina exhibits a protonic conduction ($10^{-5} \text{ohm}^{-1} \text{cm}^{-1}$ at room temperature) much higher than that of the β -phase ($10^{-11} \text{ohm}^{-1} \text{cm}^{-1}$) (G.C. Farrington and J.L. Briant, Fast Ion Transport in Solids, North Holland, New York, 1979), and the composition is relatively stable up to about 500K. Quasielastic neutron scattering has confirmed these results. To obtain further details of the location and number of the protons, neutron diffraction data for hydrated hydrogen β'' -alumina were collected at three temperatures: 110K, 300K and 620K.

The compound is rhombohedral, space group $R\bar{3}m$, and the lattice parameters in the hexagonal unit cell are:

T = 110K ; a = 5.625(4) Å ; c = 34.182(36) Å
 T = 300K ; a = 5.626(8) Å ; c = 34.234(34) Å
 T = 620K ; a = 5.630(13) Å ; c = 33.852(47) Å

Thermal gravimetric analysis shows that approximately 64% of H_2O is weakly bound and desorbed at 580K (W.L. Roth, M. Anne, D. Tranqui and A. Heidemann, Fast Ion Transport in Solids, North Holland, New York, 1979); this is consistent with the important decrease of the c-parameter between room and high temperature.

At low temperature, the composition found by neutron diffraction is $1.64H_2O \cdot 0.49MgO \cdot 5.18Al_2O_3$ per spinel-block.

Essentially, one hydrogen atom is covalently bonded to an

07.3-05 NEUTRON AND X-RAY STUDIES FOR $Na^+\beta''$ ALUMINA STABILIZED WITH Mg^{2+} OR WITH $Mg^{2+}-Li^+$. By D. Tranqui and M. Anne, Laboratoire de Cristallographie, C.N.R.S., 166X, 38042 Grenoble Cedex, France, and W. L. Roth and B. Dunn, General Electric Research and Development Center, P.O. Box 8, Schenectady, NY 12301 U.S.A.

Measurements of conductivity versus temperature for $Na^+\beta''$ alumina stabilized with Mg^{2+} or with mixed $Mg^{2+}-Li^+$ have shown significant difference between the two compounds: The $\ln(\sigma T)$ plot for the mixed compound consists of two straight lines with activation energies of 0.16 eV below 135°C and 0.10 eV above this temperature whereas that of the Mg^{2+} stabilized is nearly constant (0.32 eV) below 135°C and decreases smoothly to reach ~ 0.10 eV at 390°C. It has also been observed that the conductivity of the mixed phase is slightly higher than that of the Mg^{2+} phase, at least in the low temperature range.

Mg^{2+} and $Mg^{2+}-Li^+$ stabilized $Na^+\beta''$ alumina are rhombohedral, space group $R\bar{3}m$ with the following a and c hexagonal unit cell parameters:
 a = 5.625 Å ; c = 33.601 Å for Mg^{2+} , $Na^+\beta''$ alumina
 a = 5.616 Å ; c = 33.726 Å for $Mg^{2+}-Li^+$, $Na^+\beta''$ alumina.
 Both X-Ray and neutron diffraction data at room temperature indicated that the average bond length Al-O of the tetrahedral site Al(2) in the spinel block is significantly longer (1.849 Å) than that in the $Mg^{2+}-Li^+$ stabilized phase (1.839 Å), suggesting that the Al(2) site occupancy (by Al^{3+} , Mg^{2+} and Li^+) has been modified by Li^+ insertion. However the lithium positions are still unknown. Further neutron data refinements are underway in order to determine their location.

On the other hand the Na^+ concentration in the conduction plane is much higher (0.34) in the $Mg^{2+}-Li^+$ compound than in the Mg^{2+} compound (0.28).

Thermal expansion measurements of unit cell constants from room temperature to 450°C have shown a strikingly different behaviour between the two compounds: all para-