C-90

05. PHYSICAL PROPERTIES AND STRUCTURE

05.1-33 THE MODULATED STRUCTURE OF QUARTZ INTERMEDIATE PHASE BETWEEN \( \alpha \) AND \( \beta \) PHASES. By H. Gouhara and N. Kato, Department of electronics, Nagoya University and Department of Physics, Meijo University, Nagoya, Japan.

Recently, it has been revealed that quartz has an incommensurate phase (IP) between \( \alpha \) and \( \beta \) phases (H. Gouhara, Y. M. Li and N. Kato; J. Phys. Soc. Jpn. 52 (1983) 2391). G. Dolino, J. P. Bachheimer and C. B. Zepf; Solid State Commun. 25 (1978) 295). The structural change occurs on four levels of spatial scale from \( \delta = 10^{-1} \) cm. (K. Kato and K. Gouhara; Jpn. J. Appl. Phys. 25 (1986) 177). The purpose of this article is to elucidate the modulated structure of IP based on our data obtained by the fine-beam Laue method. Group theoretical considerations tell us that so-called \( \Sigma R \)-mode of the thermal vibration is frozen. Many authors, recalling the transition between \( \alpha \) and \( \beta \) in the present case, consider that \( \beta \)-mode is predominant. However, our observed intensities of satellites fit primarily to an acoustic transverse vibration (\( \omega \))-mode as pointed out previously (H. Grimm and B. Dorner; J. Phys. Chem. Solids, 34 (1983) 367). Questions, therefore, are whether alternatively \( \beta \)-mode can explain the observed intensity or what extent of \( \beta \)-mode is involved. The satellite intensity \( I(q) \) having the modulation vector \( q \) must be proportional to the square of the structure factor given by

\[
I(q) \propto |F(q)|^2 \quad (1)
\]

where

\[
F(q) = \sum_{k \in \Gamma} e^{i(q \cdot R_k)} \cdot f_k \quad (2)
\]

(K. Gouhara and N. Kato; J. Phys. Soc. Jpn. 52 (1983) 2868). \( q \) : Modulation vector. \( (1,1,1) \) and \( \delta \) : The reflection vector. \( F \) : The displacement amplitude. \( \delta \) : The average position of \( k \)-th atom.

Three models are examined. \( \beta \) is a purely transversal acoustic vibration with a single parameter \( u \) (amplitude). Three modes with \( q/v \leq \Sigma R \) (approximation) exist in real space. B is a purely optical vibration of \( B \) symmetry. For reducing parameters, Grim's model (H. Grimm and S. Donner; J. Phys. Chem. Solids, 34 (1957) 607) is adopted. Then all atomic displacements can be described by a single parameter \( v \) (that of Si atom). \( \Sigma R \) is a linear combination of \( E \) and \( B \) with a weight parameter \( v/v_0 \). For satellites near 22 \( L \) space, the calculated intensity is compared with our results.

In several reflections, the mixture of \( B \) mode with \( v/v_0 \) is certainly harmful. However, model \( M \) with \( v/v_0 \) seems most plausible in the case of (1, 1, 2) reflection (see Table). In conclusion, the mixing weight is 0.15 at most.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>( I(q) )</th>
<th>( I(q) )</th>
<th>( I(q) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>( u \times 10^{-4} )</td>
<td>0.189</td>
<td>0.191</td>
<td>0.375</td>
</tr>
<tr>
<td>B</td>
<td>( v \times 10^{-3} )</td>
<td>0.527</td>
<td>0.527</td>
<td>0.527</td>
</tr>
<tr>
<td>M</td>
<td>( v=0.1 )</td>
<td>0.256</td>
<td>0.206</td>
<td>0.258</td>
</tr>
<tr>
<td></td>
<td>( v=0.2 )</td>
<td>0.335</td>
<td>0.009</td>
<td>0.192</td>
</tr>
<tr>
<td>EXP. (ratio)</td>
<td>1</td>
<td>~0</td>
<td>~0</td>
<td>~0</td>
</tr>
</tbody>
</table>

05.1-34 HIGH-PRESSURE STRUCTURAL STUDIES OF THE PHASE TRANSITIONS IN PbTiO_3 AND H_2C_2O_4. By R. J. Helm, B. Ramires, R. Restori and Z. Tun, Department of Physics, University of Edinburgh, Scotland.

The phase transitions in PbTiO_3 and H_2C_2O_4 (squaric acid, or \( \text{H}_2\text{SQ} \)) both exhibit strong pressure dependence, with \( d\tau/dP \) of the order of \(-100 \text{ K GPa}^{-1} \). PbTiO_3 has a first-order ferroelectric phase transition on cooling through \( T_c = 373 \text{ K} \) at atmospheric pressure. In neutron-diffraction studies of the structural changes through \( T_c \) we have found evidence that the transition involves order/disorder behaviour in the Pb atoms. This is surprising: PbTiO_3 has long been regarded as an example of a material with a purely displacive transition. However, multi-site disordering of the Pb atoms above \( T_c \), ordering onto one of these sites below \( T_c \), could account for the large \( P \)-dependence of \( T_c \). We have now made X-ray diffraction studies of PbTiO_3, under pressure, using a diamond-anvil pressure cell (DAC), and have determined the crystal structure at a number of pressures up to \( 4.5 \text{ GPa} \). We find evidence of an anomalous \( P \)-dependence for the structural displacements in the ferroelectric phase.

\( \text{H}_2\text{SQ} \) has an antiferroelectric phase transition on cooling through \( T_c = 763 \text{ K} \) at atmospheric pressure by high-resolution neutron diffraction and have used X-ray diffraction, with a DAC, to explore the structure changes with pressure. In addition, we have now collected neutron-diffraction data at high pressures (up to 2 GPa) at room temperature and also -10 K above the pressure-reduced \( T_c \). The results show the relationship between the \( P \)-dependence of \( T_c \) and the changes in the H-bond dimensions with pressure, especially the \( H \)-site separation \( \delta \).

05.1-35 MARTENSITIC PHASE TRANSFORMATION OF SINGLE CRYSTAL LITHIUM FROM bcc TO A 9R-RELATED STRUCTURE. H. G. Smith, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831.

A neutron elastic and inelastic scattering study of single crystal bcc lithium was performed above and below the martensitic phase transformation in the vicinity of 75 K. The transformation is abrupt and the bcc lattice partially transforms to a 9R-related (\text{Sm}-type) structure, which is uniformly embedded throughout the sample. Several variants were observed and one was oriented with the (0001) zone in the scattering plane of the spectrometer. The 9R c* and a* axes of this variant are nearly along the [110] and [110] axes, respectively. The (003) and (200) reflections were broadened and shifted from their ideal positions compared to the (003) and (200) reflections, indicative of numerous stacking faults. On warming above 100 K, the sample reverts back to a single crystal with the same bcc orientation. No pronounced soft mode behavior was observed.

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