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THE LATTICE DYNAMICS OF STRONTIUM TITANATE

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Résumé. — Afin d’obtenir des informations fondamentales sur les forces interatomiques et sur les fréquences et vecteurs propres des modes normaux de vibration dans le titanate de Strontium, les fréquences de plusieurs modes normaux se propagant dans les directions [0, 0, 0], [0, 0, $\xi$], [0, 0, 0], [0, 0, 0] et [0, 0, 0] et [0, 0, 0] ont été mesurées par les techniques de diffusion inélastique des neutrons. Ces données ont été utilisées pour obtenir les paramètres de quelques modèles harmoniques de la dynamique du cristal. La dépendance en température de certains modes pourrait être obtenue avec seulement de faibles changements dans les constantes de force à courte distance. D’après ces modèles, la diffusion thermique des rayons X pour un phonon a été calculée dans plusieurs zones de Brillouin.

Abstract. — In order to provide basic information on the inter-atomic forces, and on the frequencies and eigenvectors of the normal modes of vibration in Strontium Titanate, the frequencies of several normal modes propagating in directions [0, 0, 0], [0, 0, 0], [0, 0, 0], [0, 0, 0] and [0, 0, 0] and [0, 0, 0] have been measured using neutron inelastic scattering techniques. This data has been used to obtain the parameters of several harmonic models of the crystal dynamics. The temperature dependence exhibited by certain modes could be obtained with only small changes in the short-range force constants. On the basis of these models, the one-phonon thermal diffuse X-ray scattering intensity has been calculated throughout several Brillouin Zones.

In Strontium Titanate, there are anomalously temperature dependent modes both at the zone centre and at the zone boundary. The former is responsible for the dielectric properties and the latter for the 105 $^\circ$K phase transition. Before understanding of the properties of these modes at a microscopic level can be achieved and before calculation of many of the properties of ferroelectrics can be attempted, it is essential to have a knowledge of the interatomic forces and of frequencies and eigenvectors of the normal modes of vibration. Using neutron inelastic scattering, the zone centre [$I_{1,2}$] soft mode and the lattice dynamics of SrTiO$_3$ have been investigated [1], while there have been several studies made of the R-point [$I_{2,3}$] soft mode which precipitates at the 105 $^\circ$K [antiferroelectric] phase transition [2], [3], [4].

In this paper we report further measurements of many more of the frequencies of the normal modes; model calculations have been carried out which we hope will lead to a fuller understanding of the lattice dynamics of this substance.

The experiments were carried out using triple-axis crystal spectrometers at the N. R. U. reactor of A. E. C. L., Chalk River, Canada, and at the DIDO reactor of U. K. A. E. A., Harwell, U. K. The series of experiments at Chalk River was performed on a single crystal boule of Strontium Titanate held with a [$I$, 1, 0] axis vertical, using both « Constant $Q$ » and « Constant Energy » techniques and with both constant and variable energy incident neutrons. In this way, fairly complete information was collected, at 90 $^\circ$K and 297 $^\circ$K, on modes with frequencies less than 15 THz, propagating in directions [0, 0, $\xi$],

\[\xi, \xi, 0\], $\xi, \xi, \xi\], [0, 0, 0] and $\xi, \xi, \frac{1}{2}$], whose polarization vectors were compatible with the crystal orientation. The results are shown in figure 1.

![Fig. 1. — Dispersion curves of Strontium Titanate at 297 $^\circ$K for Rigid Shell Model: 0 : present measurements ; X : reference [1]; $d$ : reference [3].](http://dx.doi.org/10.1051/jphyscol:1972245)
Careful measurements were also made of the dispersion curves in the neighbourhood of the two anomalously temperature dependent modes. The results \cite{5} indicate that, but for the $A_2$ mode discussed below, the dispersion surface is fairly isotropic about the zone-centre and R-point.

The Harwell measurements were performed to study the mode $A_2$, propagating in direction $[\frac{1}{2}, \frac{1}{2}, 0]$ between $(4, \frac{1}{2}, 0) (M_3)$ and $(\frac{5}{2}, -\frac{1}{2}, 0) (\Gamma_{25})$; to investigate this mode it is necessary to mount the crystal with a $[\frac{3}{2}, 0, 0]$ axis vertical. The measurements were made at a series of temperatures from 297 °K to 78 °K, using the same crystal as was used in the previously described experiments. The « Constant $Q$ » technique, with constant energy incident neutrons, was employed throughout.

It was found, figure 2, that the entire branch decreased in frequency with decreasing temperature and, moreover, showed little dispersion. These measurements show similar behaviour to that of the $A_2$ mode in the isomorphous material KMnF$_3$ \cite{6} where its condensation at 91.5 °K precipitates a structural phase transition.

The simplest model for the inter-ion interactions is the Rigid Ion Model \cite{7}. This model, allowing for no polarization of the ions, could be made to give only a poor representation of the data, with short-range forces restricted to neighbouring ions. The model which gave the best results was the Rigid Shell Model \cite{8} with six parameters describing the short-range interactions of Strontium-Oxygen, Titanium-Oxygen, and Oxygen-Oxygen, six describing the ionic polarizabilities and two for ionic charges. The same approximations as used in the Alkali Halide models of Woods et al. \cite{8} were made, in effect restricting all short-range forces to act through the shells.

The fitting to the experimentally determined frequencies was carried out using a non-linear least squares analysis. The fitted dispersion curves are shown in figure 1 and the parameters of this model, at 90 °K and 297 °K, in table I. As can be seen, agreement between calculated and experimental frequencies is fairly good, even in the zone-boundary directions which were not involved in the fitting of this model. As was found in the previous models of SrTiO$_3$ \cite{1}, the Titanium-Oxygen short-range forces are seen to be much larger than the others considered.

Small changes in the short-range force constants could account for the observed temperature dependence of the zone centre $\Gamma_{15}$ (ferroelectric) and R-point $\Gamma_{25}$ (antiferroelectric) modes. It proved impossible, however, to obtain the temperature dependence of $\Gamma_{25}$ and $M_3 (\frac{1}{2}, 0, 0)$ simultaneously.

As can be seen from table, the short range strontium polarizability is large and negative implying a positive shell charge for this ion. Similar behaviour was found in Rigid Shell Models of the Alkali Halides \cite{9}. In an attempt to improve upon this feature of the models, the formalism was extended to allow for isotropic radial deformations of the shells — the Deformable Shell Model \cite{10}. However, for models involving no extra parameters, agreement with experiment was not improved and, while the parameters $\alpha$ and $\delta$ could be made to assume physically reasonable values, the fit was relatively poor.

The one-phonon X-ray scattering cross-section has been calculated throughout several Brillouin Zones using the frequencies and eigenvectors calculated for the harmonic models described above. A graphical representation of the $(1, 1, 0)$ plane of the reciprocal lattice is shown in figure 3, with intensity plotted vertically. « Ridges » of intensity may be seen in high...
Table I

Strontium Titanate (Rigid) Shell Model Parameters

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Sr-O</th>
<th>Ti-O</th>
<th>O-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>297 °K</td>
<td>( A_1 )</td>
<td>( B_1 )</td>
<td>( A_2 )</td>
</tr>
<tr>
<td>90 °K</td>
<td>( A_1 )</td>
<td>( B_1 )</td>
<td>( A_2 )</td>
</tr>
<tr>
<td>Z_1</td>
<td>Z_2</td>
<td>( \alpha_1 )</td>
<td>( \alpha_2 )</td>
</tr>
</tbody>
</table>

\( \omega_{obs}^2 = \frac{1}{N\text{FREE}} \sum \frac{\omega_{calc}^2}{2 \omega_{obs} \Delta \omega_{obs}} \) = 15.03 [297 °K]  
= 11.54 [90 °K]

Strontium Titanate and it is hoped to obtain better quantitative agreement with experiment, e. g. for the temperature dependence of the mode frequencies, than has hitherto been possible [13].

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References