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LATTICE DYNAMICS AND RAMAN SPECTRA OF SrTiO₃

R. MIGONI, K. H. RIEDER, K. FISCHER and H. BILZ

Max-Planck-Institut für Festkörperforschung 7 Stuttgart-1, Federal Republic of Germany

The three independent components of the second order Raman spectra of SrTiO₃ have been measured at 300 K. They show a strong similarity to the second order spectra of SrO. Very recently, the lattice dynamics[1] and the Raman spectra of SrO have been successfully explained on the basis of a nonlinear shell model. It is shown that a modified version of this model theory can be applied to the case of SrTiO₃. The importance of the polarizability of the oxygen ion, in particular its *intra*-ionic anisotropy, for the phonon dispersion curves as well as for the Raman spectra is established. Our results are critically compared with those obtained by other authors.[2-4]

The oxidic ferroelectrica such as SrTiO₃ and BaTiO₃ show strong second order Raman spectra while those of perovskites without oxygen (e.g. KCoF₃, etc.) are very weak. The reason for this fact may be found in the unusual polarizability of the O^{2-} ion in crystals which is not a constant but increases with at least the third power of its ionic radius.[5] As a consequence, the second order Raman spectra of the earth alkali oxides (MgO, etc.) seem largely be determined by the intra-ionic polarizability of oxygen.

The concept of intra- and interionic polarizabilities has first been used by Cowley and Bruce[2] in their discussion of the alkali halides in the framework of an extended non-linear shell model. While in this case no evidence for the importance of intra- ionic polarizabilities of the anions could be obtained,[8] the work of Buchanan and co-workers[6] has led to a convincing interpretation of the high-frequency part of the Raman spectra of MgO and CaO in terms of quartic intra-ionic polarizabilities of the oxygen ion.

In order to get a sensible starting point for the analysis of the lattice vibrations and the Raman spectra of SrTiO₃ we have first tried to describe the spectra of SrO along the lines of the interpretation of MgO and CaO. We note that the strontium-oxygen distance in SrTiO₃ exceeds less than 7% that in SrO and we expect therefore, that the dynamical properties of the Sr-O (100) planes in SrTiO₃ exhibit still some similarities to those of the corresponding planes in SrO.

We have used an overlap shell model[7] with 7 parameters which considers a psuedo-polarizability at the strontium ion due to the overlap polarization between Sr and O. In contrast to the case of MgO and CaO, a small but negative shell charge at the Sr ion was found to give the best fit of the dispersion curves.[1] This model was then used in a calculation of the second order Raman spectra of SrO. The details of the formal treatment are given in the above-mentioned papers and should not be repeated here. The results are shown in Figure 1. As in MgO and CaO, the high frequency part of the scattering stems from the non-linear intra-ionic polarizability of the oxygen ion. This polarizability may be introduced via a short-range core-shell potential of fourth power in the relative shell displacements. In addition, four peaks in the Raman spectra (at 150, 390, 490 and 545 cm⁻¹) could be identified as due to the inter-ionic polarizability between strontium and its neighbouring oxygen ions. The fact that the numerical values of the two fitted parameters are consistent with a Laplace equation for the interionic polarization potential may indicate the long-range character of this electron-ion interaction.

We have then tried to use our results in SrO for an analysis of SrTiO₃. Here, we expected that the above

FIGURE 1   Second order A₁g Raman spectra of SrO at room temperature. Experimental data: Ref. 9.

mentioned strong dependence of the oxygen polariz-
ability on its radius and on the "chemical" nature of
its neighbours should lead to a large anisotropy of the
intra-ionic polarizability of oxygen in $SrTiO_3$. This is
in addition to the inter-ionic anisotropy of the polariz-
ability due to the very different force constants
between the pairs Sr-O and Ti-O.

The inspection of the existing measurements of the
lattice vibrations in $SrTiO_3$ by Stirling[3] and by Iizumi
et al.[4] exhibits large discrepancies between the results
of the two groups (see Figure 2). It is questionable,
whether this, at least partially, is due to the fact that
Stirling's high frequency measurements at 90 K are
below the anti-ferroelectric phase transition at 105 K
while those by Iizumi *et al.* are all at room temperature
like our Raman investigations. The second set of
measurements is, unfortunately, very incomplete.
Therefore, we have used our SrO model results as a
starting point and have fitted Stirling's 14 parameter
shell model to his "297 K" data by introducing one
more parameter, namely an anisotropic core-shell
force tensor for oxygen (K_{Ti}^3 and K_{Sr}^3 instead of
Stirling's K_3). The results of our fit are shown in
Figure 2. They are only slightly better than those
obtained by Stirling. The anisotropy of $\alpha(O^{2-})$ is,
nevertheless, quite remarkable. Our fit gives $K_{Sr}^3 \approx 6K_{Ti}^3$
which means that the deformability of the oxygen ion
in the direction of the titanium ions seems to be much

higher than that in the Sr-O planes. This rather un-
physical result may be caused by our fit to the experi-
mental data of Stirling (see discussion below).

For the calculation of the second order Raman
spectra we had to replace the simple quartic potential
in SrO for the intra-ionic polarizability with two para-
meters, i.e. $H_1(K) + H_2(K)\delta_{\alpha\beta}$ (Eq. 5 in Bruce and
Cowley[2]) by a more complex description using four
parameters corresponding to the anisotropy of the
oxygen position in $SrTiO_3$.

In Figure 3 our calculations are compared with the
experimental data. We have found that the higher part
of the spectrum (above 350 cm^{-1}) originates practically
only from the quartic Sr-O potential like in cubic SrO.
This demonstrates that the high frequency part of the
Raman scattering in both crystals is due to the intra-
ionic polarizability of oxygen in the SrO planes. For
the lower part of the spectrum a very small "transverse"
contribution where the relative Ti-O motion modulates
the oxygen polarizability in the Sr-O planes was used.
Adding of the other two parameters did not give any
improvement. That means that no contribution to the
Raman scattering in $SrTiO_3$ originates from a modu-
lation of the oxygen polarizability in the direction of
the neighbouring titanium ions. This supports the idea
of a strong anisotropy of the oxygen polarizability in
the Raman scattering in $SrTiO_3$ and consequently, in
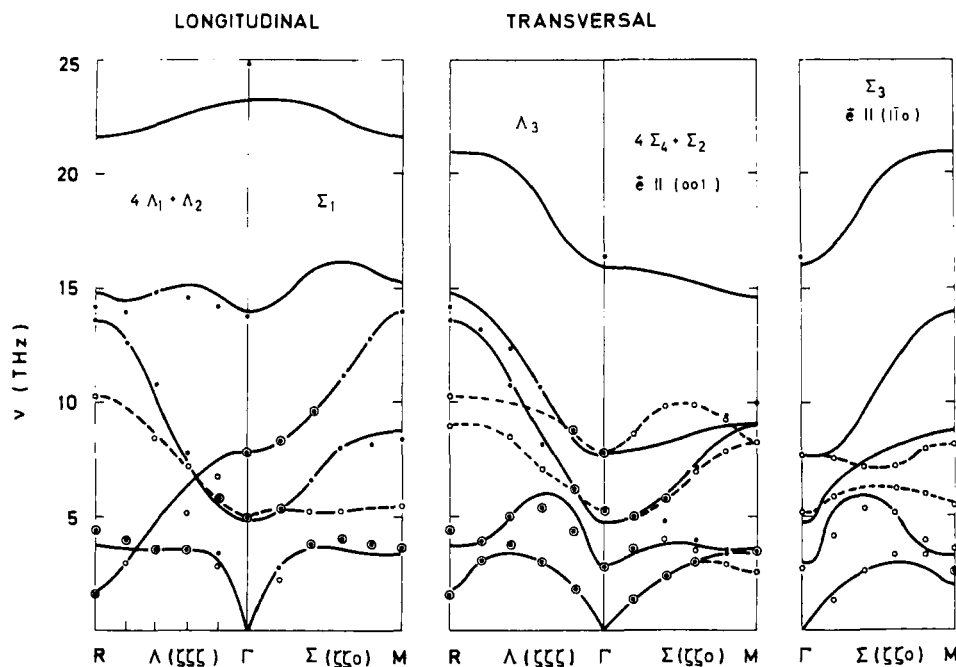other oxydic perovskites.

FIGURE 2   Dispersion curves of $SrTiO_3$ at room temperature. ooo Ref. 4,   ● Ref. 3,   ⊙⊙⊙ Ref. 3, 4 --- interpolation lines
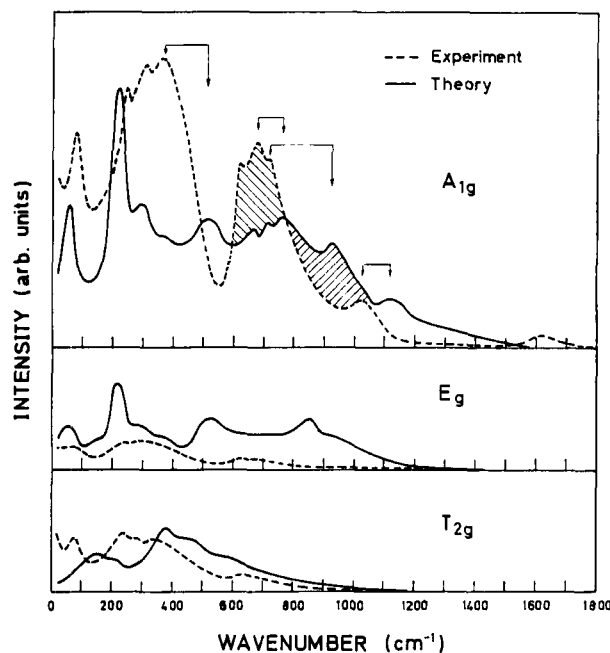Ref. 4, ——— this calculation fitted to the data of Ref. 3.

FIGURE 3   Second order Raman spectra of SrTiO₃ at room temperature.

A very disturbing point is the obvious shift of many peaks of the calculated spectra to higher frequencies as compared with the experimental peaks. Discrepancies are much larger (up to 25%) than those expected from the errors in the lattice dynamical fits (less than 10%). We have therefore estimated the lowering of the frequencies of several peaks if the experimental data of Stirling are replaced by those of Iizumi et al. (see e.g. the second lowest longitudinal branch in the (110) direction, Figure 1). Such a change of the lattice dynamics seems to bring the calculated peaks nearly in coincidence with the observed ones and gives a satisfactory description of all observed features of the Raman spectra, including approximately the ratio of intensities between different symmetries. The calculated E_g spectra show the strongest deviations from the experimental data. With respect to intensities, only a small section of the middle of the first band in Figure 3 may still be missing in our calculation which (as in SrO) could stem from inter-ionic terms.

Our Raman model differs from the used by Bruce in Sterling's paper in two important points. Firstly, no breathing deformability of the oxygen ion has been used since we feel that this is only a simulation of the overlap polarization.[7,8] Secondly, we used an *an*isotropic

intra-ionic polarizability and found this essential for the description of the data.

In conclusion, we derive at the following results:

1) The second order Raman spectra in SrO and in SrTiO₃ are governed at higher frequencies by the quartic intra-ionic polarizability of oxygen.

2) In SrTiO₃, a very large anisotropy of this polarizability reduces the scattering to that coming from the Sr–O planes. There is no contribution from the Ti–O–Ti direction.

3) The lattice vibrations of SrTiO₃ as measured by Stirling should be re-investigated. There are strong indications that the measurements by Iizumi et al. are more reliable at 300 K.

4) The layer-like behaviour of the oxygen Raman scattering in SrTiO₃ leads to the presumption that the oxygen in other situations with local anisotropies (e.g. other perovskites, surfaces, etc.) would exhibit similar scattering properties.

REFERENCES

1. K. H. Rieder, R. Migoni and B. Renker, *Phys. Rev.* **B12**, 3374 (1975).
2. R. A. Cowley, *Phys. Rev.* **4A**, 981 (1964); A. D. Bruce and R. A. Cowley, *J. Phys.* **C5**, 595 (1972).
3. W. Stirling, *J. Phys.* **C5**, 2711 (1972).
4. M. Iizumi, K. Gesi and J. Harada, *J. Phys.* **C6**, 3021 (1973).
5. J. R. Tessman, A. H. Kahn and W. Shodkley, *Phys. Rev.* **92**, 890 (1953).
6. M. Buchanan, R. Haberkorn and H. Bilz, *J. Phys.* **C7**, 439 (1974).
7. H. Bilz, M. Buchanan, K. Fischer, R. Haberkorn and U. Schröder, *Solid State Commun.* **16**, 1023 (1975).
8. M. Krauzmann, *Solid State Commun.* **12**, 157 (1973).
9. K. H. Rieder, B. A. Weinstein, M. Cardona and H. Bilz, *Phys. Rev.* **B 8**, 4780 (1973).

NOTE ADDED IN PROOF

Very recently, Dr. Stirling has confirmed his previous measurements (private communic.). This leads us to a modified interpretation of the experimental data (Migoni, Bilz and Bäuerle, to be published).