Lattice dynamics of Sr$_2$TiO$_4$

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Abstract. Lattice dynamics of Sr$_2$TiO$_4$ is investigated by means of inelastic neutron scattering and Raman scattering experiments. The phonon density of states is experimentally determined by inelastic neutron scattering experiment and all the peaks except the one at 88 cm$^{-1}$ can be attributed to some optical modes, whereas the peak at 88 cm$^{-1}$ is probably due to the acoustic phonons at the zone boundary. Raman scattering experiments done at low temperature reveal that the explicit contribution to the anharmonicity from the thermal population of the vibrational levels should be stronger for the high energy A$_{1g}$ mode at about 570 cm$^{-1}$ than for the other Raman active modes. This contribution increases anomalously with the temperature due to a quartic anharmonic contribution.

1. Introduction
Sr$_2$TiO$_4$ crystallizes in the K$_2$NiF$_4$ structure and is a wide-gap semiconductor with bandgap slightly larger than the one of SrTiO$_3$ [1, 2]. Sr$_2$TiO$_4$ is a compound closely related to the perovskite compound SrTiO$_3$ and is composed of SrO layers separating SrTiO$_3$ block layers. Hence, it is interesting to compare the physical properties of both compounds. Sr$_2$TiO$_4$ has large dielectric constant which is, however, smaller than the one of SrTiO$_3$ [2, 3]. The dielectric constant also varies much less with temperature than in the case of SrTiO$_3$ [2, 3]. This makes this compound interesting for possible industrial applications as, for example, alternative gate oxide in MOSFETs [2]. Another interesting characteristic of Sr$_2$TiO$_4$ is its lower thermal conductivity compared to SrTiO$_3$, which could make Sr$_2$TiO$_4$ attractive for thermoelectric applications if its electronic properties can be improved [4]. For these reasons, a better understanding of the differences between this compound and SrTiO$_3$, and a better knowledge of its lattice dynamics is necessary. In this communication, we report on new experimental studies aimed at understanding the lattice dynamics in Sr$_2$TiO$_4$. We have performed Raman scattering experiments at different temperature and inelastic neutron scattering (INS) experiment on powder Sr$_2$TiO$_4$ samples.

2. Experimental details
The synthesis conditions for obtaining single-phase Sr$_2$TiO$_4$ in the limit of XRD detection are the following: after mixing and ball-milling stoichiometric amounts of SrCO$_3$ and TiO$_2$, the mixture is calcined at 1200 °C for 12 h; the resulting product is ball-milled and sintered at 1100 °C for 12 h. Raman spectra were excited with an Ar$^+$ laser (Lambda=514.5 nm) and analyzed using a Jobin-Yvon T64000 spectrometer equipped with a cooled CCD (T=140 K). All the spectra were obtained in a back scattering geometry using a microprobe device that allows the incident light to be focused on the
sample as a spot of about 2 micrometer in diameter. The low-temperature measurements were performed using a helium microstat Oxford with a temperature stability of 0.5 K.

The INS experiments have been performed at ILL in Grenoble on the IN6 spectrometer. The wavelength used was 0.41 nm, permitting an energy resolution of 1.5 cm$^{-1}$ in the energy range 0-100 cm$^{-1}$. The phonon density of states (pDOS) has been obtained from INS spectrum using the incoherent approximation [5]. Multiphonon corrections have not been considered.

3. Experimental results

We report in figure 1 the experimental pDOS obtained from INS experiments together with the Raman spectrum of Sr$_2$TiO$_4$ at room temperature. There are four first order Raman modes at 122 cm$^{-1}$, 204 cm$^{-1}$, 284 cm$^{-1}$ and 574 cm$^{-1}$ in good agreement with previous results in the literature [6-8]. The peaks at about 425 cm$^{-1}$ and 700 cm$^{-1}$ should correspond to the second order Raman modes. As we can see in figure 1, there is a correspondence between bands of the pDOS with the first order Raman peaks at 122 cm$^{-1}$ and 284 cm$^{-1}$. This is what we expect for optical modes. Also, there are two infrared modes which correspond to the peaks at 175 cm$^{-1}$ and at about 507 cm$^{-1}$ in the pDOS [6-8]. Due to the poor resolution of 40 cm$^{-1}$ at the energy range between 600 and 800 cm$^{-1}$ and to the possible presence of multiphonon contribution, it is not possible from our experimental pDOS to resolve the broad infrared band observed at 700 cm$^{-1}$ in the literature [6-8].

We also should remark that there is no optical mode below 100 cm$^{-1}$ in Sr$_2$TiO$_4$, contrary to the case of SrTiO$_3$ [6-8]. Therefore, the peak at 88 cm$^{-1}$ (11 meV) should be due to the transverse acoustic phonons at the zone boundary. Indeed, that has been seen in lot of materials and notably in the case of La$_2$CuO$_4$ for which a peak has been found in the pDOS at 97 cm$^{-1}$ (12 meV) [5] and has been attributed to the acoustic phonons at the zone boundary in agreement with theoretical calculations [5,9]. Also, in the INS spectrum of BaTiO$_3$, there is a peak at 78 cm$^{-1}$ due to acoustic phonons [10]. We also note that the Debye model for which the pDOS behaves as $\omega^2$ is valid up to the energy of 65 cm$^{-1}$ (8 meV) in our sample. Finally, we can not compare the pDOS of Sr$_2$TiO$_4$ with the one of SrTiO$_3$ because there is no published experimental report of experimental pDOS in powdered SrTiO$_3$ and we note that the pDOS of Sr$_2$TiO$_4$ is very different to the one of BaTiO$_3$ [10].

We have measured the temperature dependence of the Raman spectra between 20 and 300 K. In figure 2, we compare these spectra at 20 and 300 K. The temperature dependence for the two E$_g$ modes are inside the experimental error (1 cm$^{-1}$), whereas there is significant temperature dependence

![Figure 1. Phophon density of states as determined by INS experiments and Raman spectrum of Sr$_2$TiO$_4$ at room temperature](image-url)
for the two $A_{1g}$ modes (see figures 3 and 4). These observations confirm the previous experiment at 77 K and room temperature performed by Burns et al [8] on Sr$_2$TiO$_4$, although the temperature dependence of the high energy $A_{1g}$ mode is found to be weaker in our measurements.

![Figure 2](image-url). Raman spectra of Sr$_2$TiO$_4$ at room temperature and at 20 K.

![Figure 3](image-url). Temperature dependence of the low energy $A_{1g}$ Raman mode.

![Figure 4](image-url). Temperature dependence of the high energy $A_{1g}$ Raman mode.

There are two different contributions to the thermal variation of the position of the Raman modes due to the anharmonicity: one implicit contribution and one explicit contribution [11]. The first one corresponds to the contribution of the volume dependence of the Raman modes in the quasi-harmonic contribution. It can be deduced from the knowledge of the pressure dependence of the position of the Raman modes, of the bulk modulus and of the thermal expansion. The second contribution is the anharmonic contribution coming from the thermal population of vibrational levels. For Sr$_2$TiO$_4$, the pressure dependence of these Raman modes is positive. As a consequence, these modes harden with decreasing volume [12]. Hence, if the quasi-harmonic contribution (i.e. the volume contribution) to the temperature dependence of the Raman mode dominated, we would expect that all the Raman modes behave as the low-energy $A_{1g}$ mode. All Raman modes would have a blue shift when the temperature decreases and, thus, the volume decreases. However, this is not the case for the $E_g$ modes and notably for the high energy $A_{1g}$ mode. That means that for all these modes and especially for the high energy $A_{1g}$ mode, the explicit contribution to the thermal variation of the Raman modes is larger compared to the case of the low energy $A_{1g}$ mode and increases with the temperature. Such a behavior is quite unusual but has already been observed for the $A_{1g}$ mode at 612 cm$^{-1}$ of the rutile TiO$_2$ [13]. In the case
of TiO$_2$, it was suggested that the anomalous temperature dependence of the A$_{1g}$ was due to quartic anharmonicity and not to cubic anharmonicity [13]. We can make the same proposal for the high energy A$_{1g}$ mode of Sr$_2$TiO$_4$. It is interesting also to note that this A$_{1g}$ mode implies O atoms constituting an octaedra in TiO$_2$ and that the high energy A$_{1g}$ mode of Sr$_2$TiO$_4$ implies essentially the motion along c of the two O atoms at the top and bottom of the octaedra [6, 8]. Finally, the large FWHM of the high energy A$_{1g}$ mode compared to the ones of other Raman modes is also another indication that the thermal population of vibrational levels is the dominant mechanism of the temperature dependence of this mode. However, at this investigation stage, we can not conclude upon the anharmonicity of the different Raman modes in detail. High quality thermal expansion and bulk modulus experiments are needed for quantifying the different contributions to temperature dependence of the different modes and also for determining their Grüneisen parameters. In this case, we could quantify the explicit contribution and thus also deduce the implicit contribution due to the anharmonicity for these Raman modes.

4. Conclusion
We have investigated the lattice dynamics of Sr$_2$TiO$_4$ by means of INS and Raman scattering experiments. All the bands found in the pDOS determined by INS experiments could be assigned to optical modes except the one at 88 cm$^{-1}$. This peak is probably due to the acoustic phonons at the zone boundary. Raman scattering experiments reveal weak temperature dependence for the E$_g$ modes, but on the other hand a strong temperature dependence of the A$_{1g}$ mode. The position of the low energy A$_{1g}$ mode decreases when the temperature increases as expected from the volume dependence of this mode. On the other hand, the position of the high energy A$_{1g}$ mode increases with the temperature and we attribute this anomalous behavior to the strong quartic anharmonic contribution from the thermal population of the vibrational levels for this mode, as in the case of the A$_{1g}$ mode of TiO$_2$.

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