

High-resolution infrared spectroscopy of hydrogen impurities in strontium titanate

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A high-resolution infrared spectroscopic investigation of structure related to the O-H dipole stretching mode (around 3500 cm^{-1}) was carried out in SrTiO_3 . We discuss various models for the position of the hydrogen impurity in the matrix and justify the position that we have suggested in a previous paper. With this new assignment, we discuss the 16 highest intensity peaks observed at low temperature. The high-energy satellites are interpreted as arising from the absorption of hydrogen impurities located on inequivalent sites. These sites are made inequivalent by a combination of the antiferrodistortive transition at 105 K and the ferroelectric fluctuations that become important when the temperature decreases.

I. INTRODUCTION

Recently, some effort has been devoted to study the behavior of hydrogen as an impurity in the oxygen perovskites (ABO_3) and in similar compounds. The concentration of hydrogen impurities and also their position in the unit cell are important considerations for applications in nonlinear optics and electrooptics as well as for holographic storage. One of the easiest techniques for such a study is infrared spectroscopy from which the hydrogen impurity can be characterized, mainly via the stretching mode of the O-H dipole whose frequency occurs around 3500 cm^{-1} . Such a study was done on SrTiO_3 ,¹⁻⁵ BaTiO_3 ,^{6,7} KNbO_3 ,⁸ KTaO_3 ,^{9,10} LiNbO_3 ,¹¹ and TiO_2 .¹² Amongst these, strontium titanate is an interesting case. It has an antiferrodistortive phase transition around 105 K involving a rotation of the oxygen octahedra with respect to the strontium cage. Furthermore, it is an incipient ferroelectric compound with a static dielectric constant increasing to more than 10 000 at low temperature. In this paper, we present high-resolution infrared spectra of the O-H stretching vibration mode in SrTiO_3 as a function of temperature. We analyze these results (up to 16 resolved peaks at low temperature) in the context of a model involving both the antiferrodistortive transition and the ferroelectric fluctuations.

Kapphan *et al.*^{1,2} analyzed the behavior of the high-intensity peaks on monodomain samples of SrTiO_3 . From this analysis, they deduced a position for the hydrogen

impurity in the perovskite structure. It was placed along the oxygen-oxygen sides of the oxygen octahedra. These results were based on an analysis of the O-H stretching dipole peak at high temperature, of its splitting into three components at low temperature due to the structural distortion and of their behavior as a function of polarization and electric field. This interpretation was found to be incorrect by Jandl *et al.*⁵ since this position would lead to four large low-temperature peaks instead of the three observed. Brebner *et al.*⁴ proposed an axial position which was incompatible with the results of Kapphan *et al.*¹ Finally, Jandl *et al.*⁵ proposed a configuration in which the hydrogen ion lies between oxygen and strontium atoms. This position is compatible with all the results known at the present time.

In this communication, we discuss the behavior of the high-intensity components of the O-H dipole infrared absorption as a function of temperature. We present our model for the position of the hydrogen atoms which is fully compatible with previous experiments done on monodomain samples under electric field with polarized light. We also present the temperature dependence of the smaller intensity, high-energy replicas of these main peaks. These replicas have often been interpreted as related to an O-H dipole in the neighborhood of a crystal defect (oxygen vacancy or metallic impurity). Rather, we interpret the 16 low-temperature highest-intensity peaks as due to the crystal distortion related to the rotation of the oxygen octahedra combined with the fluctuations of the ferroelectric soft mode.

II. EXPERIMENTAL RESULTS

We used nominally pure single crystals obtained from Commercial Crystal Laboratories. They were cut and polished in rectangular slabs ($3 \times 7 \times 9$ mm³) with sides parallel to [100]. Transmission measurements were made at normal incidence at temperatures ranging from 14–790 K. The high-temperature measurements, for which we did not need high resolution, were performed on a

Perkin-Elmer model 180 spectrometer, the best resolution being 0.5 cm⁻¹. Our high-resolution (0.05 cm⁻¹) low-temperature spectra were obtained from a Fourier-transform spectrometer, Bomem DA3.002 model. High temperatures ($300 < T < 790$ K) were obtained using a specially designed double chamber oven inserted into the Perkin-Elmer spectrometer. A CTI closed-cycle refrigerator was used to obtain the low temperatures. The precision of the temperature measurements was ± 0.5 K.

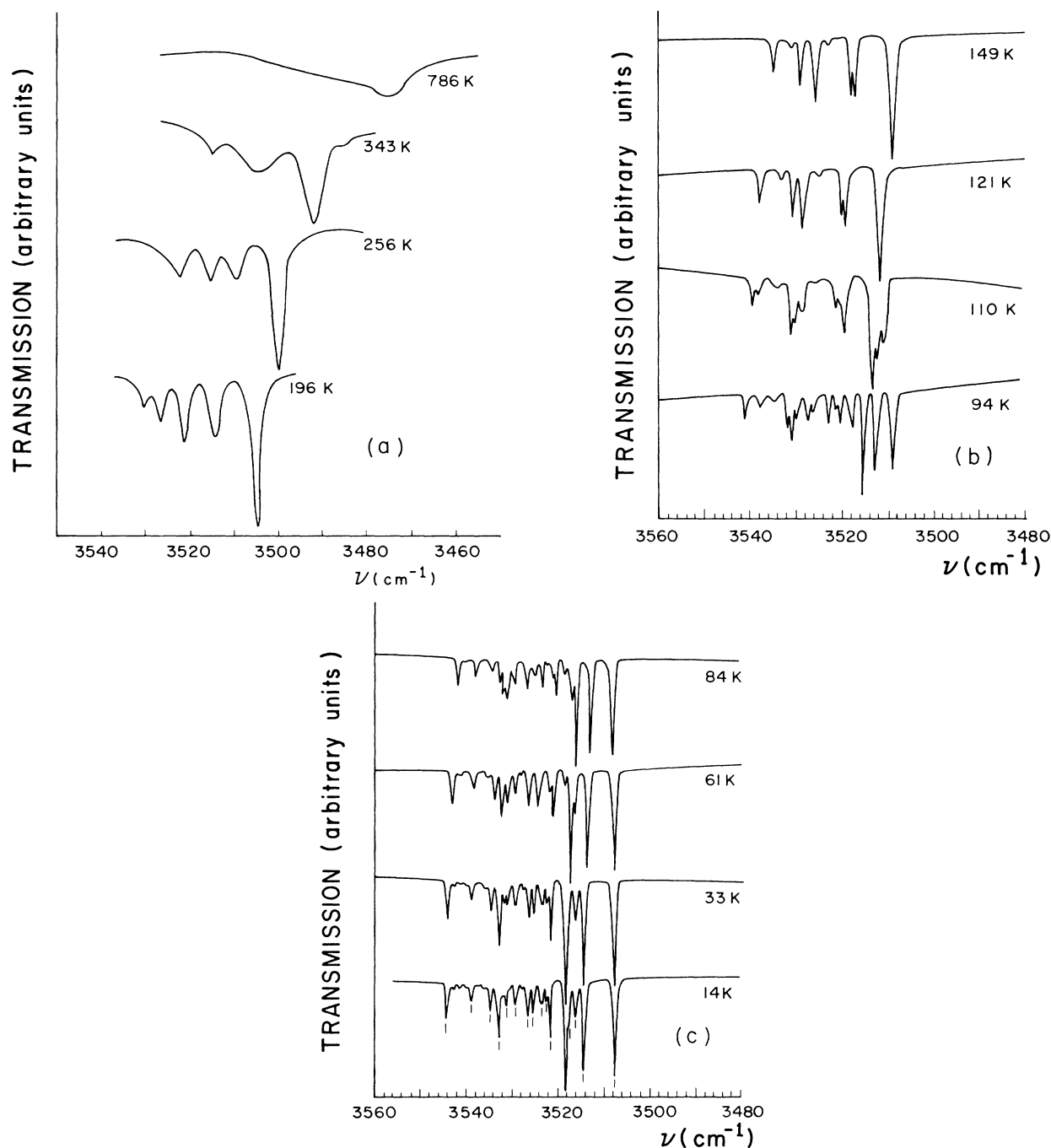


FIG. 1. SrTiO₃ infrared transmission around the O-H stretching vibration frequency. (a) shows spectra for 786, 343, 256, and 196 K; (b) for 149, 121, 110, and 94 K; and (c) for 84, 61, 33, and 14 K.

Since even a very small strain can shift the absorption structures by 1 to 2 cm^{-1} , our best sample was permanently mounted on a holder in order to avoid strains. It is known that a weak uniaxial stress can shift the transition temperature and change the second-order transition into a first-order one. Polarization of light had no effect on the spectrum since in the low-temperature phase we did not have monodomain samples.

In Fig. 1(a) there appear typical transmission spectra in the 3500-cm^{-1} region for $T=786, 343, 256$, and 196 K. These spectra were obtained with the Perkin-Elmer spectrometer. In Fig. 1(b) appear spectra for $T=149, 121, 110$, and 94 K while in Fig. 1(c), we plot spectra for $T=84, 61, 33$, and 14 K. The last two figures were obtained from Fourier transform spectroscopy (resolution of 0.05 cm^{-1}). In Fig. 2, we plot the O-H absorption frequency as a function of temperature. The experimental data appear as dots. The curves passing through them help one to follow the evolution with temperature. They will be discussed later. A single peak is obtained for temperatures higher than 700 K while sixteen peaks are resolved at low temperature, from 94 K down to 14 K (these 16 peaks are indicated by vertical bars at 14 K). At the lowest temperature, some additional low-intensity absorption peaks can be seen but they are different from the others because of their very low intensity and because they do not emerge from a wider high-temperature peak. The hydrogen concentration in the crystal can be estimated from the oscillator strength of the O-H dipole obtained in TiO_2 by Johnson *et al.*¹³ It is around 10^{18} hydrogen atoms/ cm^3 .

As the absorption frequency of the O-H dipole is a very good probe of the microscopic order, we have measured infrared absorption at low temperature, under a magnetic field. This was done to test predictions that the transition temperature could be shifted as much as 10% for a magnetic field of 20 T.¹⁴ Such a variation should be visible as a shift in low-temperature absorption frequency and our sensitivity should be better than that obtained from neutron diffraction. We have applied a 7-T magnetic field and no variation in amplitude or in frequency of the mode was observed. This confirms the results obtained by Comès *et al.*, using neutron diffraction.¹⁵

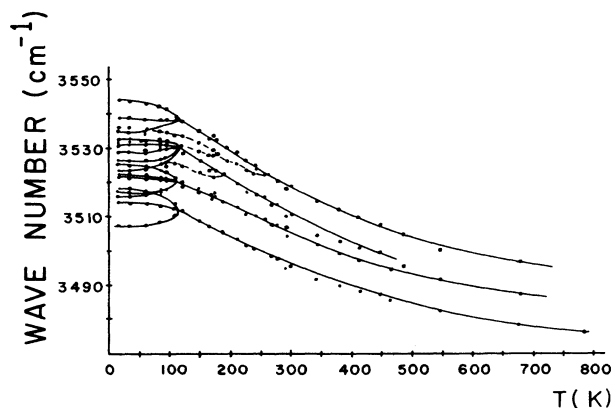


FIG. 2. Frequencies of the O-H stretching mode in SrTiO_3 , as a function of temperature.

III. DISCUSSION

In this section, we present a model that we use to interpret the present results and also other existing measurements done under electric field or using polarized light on monodomain samples for the low-temperature phase.¹⁻³ First, we summarize the latter measurements. It was first observed by Klukhuhn *et al.*³ that the highest-intensity, low-energy peak observed at high temperature was split into three components by the antiferrodistortive transition occurring at $T_c=105$ K. These peaks correspond to the O-H stretching vibration. Kapphan *et al.*¹ studied the effect of a static electric field on these three peaks. Their measurements were done both on hydrogenated and deuterated samples and they obtained comparable results for both types of samples (with the exception of the shift in frequency from around 3500 to 2600 cm^{-1}). They worked on samples under a $[1\bar{1}0]$ stress sufficient to produce monodomains with rotation axis (c axis) parallel to the $[001]$ direction. This stress did not change the intensity, the position or the multiplicity of the three peaks in the low-temperature phase.

First, they observed that for light propagating in the $[110]$ direction, a polarization along $[001]$ decreased substantially the middle component, while a $[1\bar{1}0]$ polarization doubled its intensity. They also found that for light propagating along the c axis, a static electric field along $[110]$ splits the three components each into two parts if the light is polarized along the electric field, but splits only the two outer components if the polarization is perpendicular to the static field. For light propagating in the $[110]$ direction, the same electric field splits the two outer components if the light polarization is along the c axis (and the middle component is nearly absent) while for polarization along the stress direction, the middle component stays unchanged while the two other components split in two.

Kapphan *et al.*¹ interpreted these results by proposing a model for which the hydrogen is positioned along the O—O bonds of the oxygen octahedra. This configuration is illustrated in Fig. 3. However, there is a problem with this microscopic model. We find that, in addition to the three inequivalent positions of the hydrogen atoms reported, a fourth position must be considered. This fourth has been drawn on Fig. 3 and has been labeled as IV. This position is energetically different from that labeled III because, when the oxygen octahedra rotate about the c axis at the phase transition, one hydrogen atom (IV) moves away from the two nearest corner strontium atoms while the other (III) moves toward the same strontium atoms. Their model would then predict a splitting of the main absorption peak into four components instead of three, for $T < T_c$. The interpretation of the other experiments would also have to take care of this additional site and results different from those observed are predicted.

To account for these results, Jandl *et al.*⁵ introduced a new model: hydrogen atoms were placed on the faces of the cube, between the oxygen and strontium atoms. The representative new positions are indicated on Fig. 4 as position 1, 2, 3, 4, and their primes (the primes indicate additional inequivalent positions when an electric field is

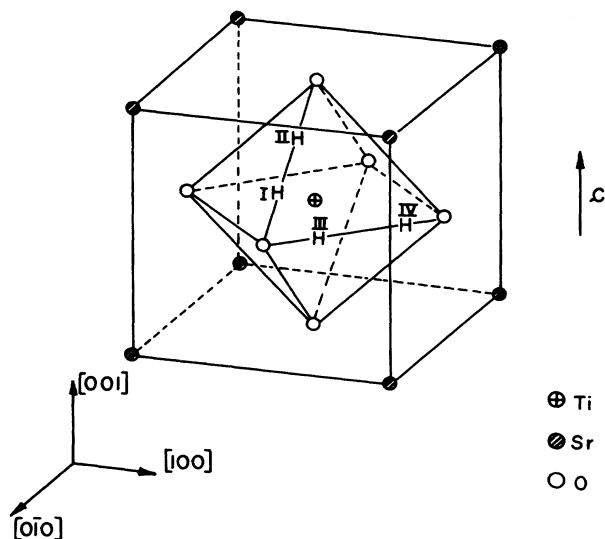


FIG. 3. Location of the hydrogen atoms in the SrTiO_3 unit cell, according to Kapphan *et al.* (Ref. 1).

present). First, for $T < T_c$, a rotation of the oxygen octahedra occurs and three inequivalent positions are created: 1 is equivalent to 2; 3 and 4 are different from one another and from 1 and 2. A splitting into three components is predicted as observed. If light polarized in the $[1\bar{1}0]$ direction is used on monodomain crystals, the same three components are observed. If light polarized in the $[001]$ direction is used, only two peaks are seen: The absorption corresponding to hydrogens 1 and 2 is no longer visible, the bonds being perpendicular to the polarization of the incident radiation E_L . We thus assign the central peak to hydrogen position 1 and 2 and the outer components to positions 3 and 4. These outer components

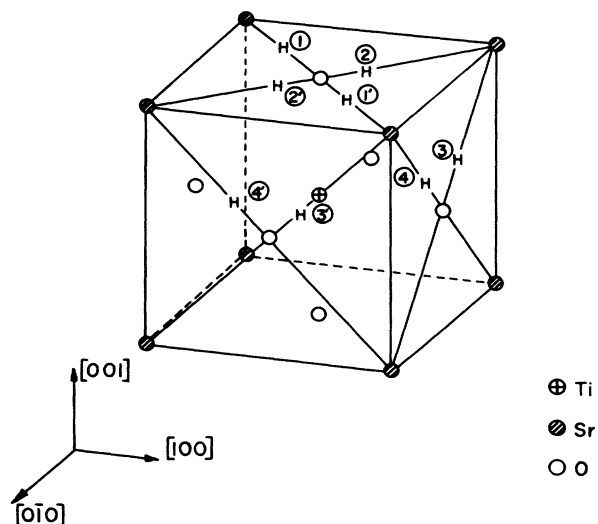


FIG. 4. Location of the hydrogen atoms in the SrTiO_3 unit cell, according to the present paper.

will appear through the projection of the O-H vibration on the electric field E_L . The projection angle being 45° in the $[001]$ case and 60° for the $[110]$ case, the absorption intensity should double for the polarization along the c axis, as suggested by the experimental results. Our model is thus perfectly compatible with the polarization experiments.

The action of an electric field on a polar crystal is twofold: First, it results in a splitting of the electric dipole absorption by creating inequivalent (relative to the orientation with respect to the electric field) hydrogen sites and, second, it results in a displacement of the ionic positions, which may be particularly important, because of the soft mode existing in such crystals. We do not know for the moment which mechanism is predominant in SrTiO_3 but both lead to the same results in the case of our model (Fig. 4). First, we consider the case of light propagating along the c axis with applied electric field E_A and E_L pointing in the $[110]$ direction. In this case, it is found that each peak of the triplet splits into two components. These six absorption peaks correspond to six inequivalent positions of the hydrogen atoms. 3 and 4 remain inequivalent but become different from 3' and 4'. This accounts for the splitting of the outer components. The positions 1 and 1' are not visible because they have no components along E_L (except for second-order effects due to the oxygen rotation). The positions 2 and 2' become inequivalent and account for the splitting of the central peak. We predict that this splitting is twice that of the outer peaks since the angle between E_A and the O-H bond is 60° in the latter case and 0° for the former. If E_A stays in the same direction but E_L points in a perpendicular direction $[1\bar{1}0]$, it is observed that the splitting of the outer peaks stays the same while the central peak is not split. This change of direction of E_L has no effect on positions 3, 3', 4, and 4', the predicted corresponding absorption being the same in both cases. However, as E_L is in the direction of the 1 and 1' dipoles, 2 and 2' cannot be seen, being perpendicular. As E_A is orthogonal to the direction of 1 and 1', it has no effect on their absorption and no splitting is observed for the central peak. For light propagating along the $[110]$ direction and the electric field lying in the same direction, we can carry out the same type of analysis. If E_L is along the c axis, it is perpendicular to the dipole 1, 2, 1', 2' the middle component cannot be seen. The outer components are split in two because of E_A . If E_L is in $[1\bar{1}0]$ direction, 2 and 2' are not seen being perpendicular to the field. 1 and 1' are seen as degenerate, E_A being orthogonal to them. This produces a degenerate inner component. The two outer components are then split into two by E_A , as observed. From this analysis, our model is seen to be compatible with all the measurements reported.

Concerning the high-energy satellite bands, we proposed a new model capable of explaining the observed data and compatible with the previous analysis of the high-intensity peaks.⁵ In this paper, we develop this model further and use it to interpret our new high-resolution spectra. This model consists in interpreting the high-energy replica as arising from the ferroelectric fluctuations. Such fluctuations are known to be important in

strontium titanate.¹⁶ Also in the same reference, it was found that these fluctuations favor a polarization in the [100] direction (and not in the [111] direction as in KTaO_3). This is probably related to the 105-K transition which defines a nonequivalent axis in the [100] direction, at low temperature. These ferroelectric fluctuations occur at a low frequency relative to the dipole vibrations: Their typical energy is around 100 cm^{-1} as compared to the dipole vibration energy which is 3500 cm^{-1} . As such, the polarization fluctuations appear as static with respect to the dipole vibrations. Our approach is thus to consider the high-energy structures as due to replica of the high-intensity peaks but shifted in energy due to the ferroelectric fluctuations. We will now analyze the different possibilities that can occur.

These possibilities appear in Fig. 5. The hydrogen atoms are placed between the strontium and the oxygen atoms, as described and justified in the beginning of this section. For $T > 105 \text{ K}$, four inequivalent hydrogen positions have been found [Fig. 5(a)], one corresponding to equilibrium and the others corresponding to the ferroelectric configuration. For $T < T_c$, each of the four peaks are predicted to split into several components. First, the high-intensity equilibrium peak splits into three, as previously discussed [Fig. 5(b)]. Second, consideration of Figs. 5(c) and 5(d) shows that the peak corresponding to the hydrogens on the top and bottom faces of the unit cell under the ferroelectric fluctuation splits into three parts as an effect of the hydrogen rotation. It can also be seen from these figures that the two high-temperature peaks corresponding to the dipoles along the lateral faces of the cubes (one for the upper hydrogens and one for the lower) split each into five components as an effect of the 105 K transition. As a result, four peaks are predicted at high temperature while 16 are predicted at low temperature: two groups of three and two of five. These conclusions agree well with the experimental spectrum, as it can be seen in Fig. 2 on which the lines have been drawn according to this model. The very low-intensity peaks have been dis-

carded. Some extra lines are seen between 90 and 300 K. They can be assigned either to ferroelectric fluctuations corresponding to polarization in other directions (along [110] or [111] rather than [100]) or to ferroelectric domains in which a virtual antiferrodistortive transition had occurred. These fluctuations disappear at low temperature with the appearance of a c axis that defines a privileged direction.

One would expect the intensity of these replicas to increase as the temperature decreases since the ferroelectric fluctuations become more important because of the softening of the phonons. However, it is known that the static dielectric constant also increases drastically at low temperature, screening the dipole. The combination of these two effects can explain the very small temperature dependence observed. However, no detailed experimental or theoretical analysis has been attempted since the occupation probabilities of the different sites and the oscillator strengths are unpredictable. Also, it is observed that the relative intensity of the satellites can vary from sample to sample. This can be related to the sensitivity of the behavior of the ferroelectric fluctuations to the distribution of defects and to the stress applied on the sample. For example, it is known that a small amount of barium in SrTiO_3 is enough to make it ferroelectric. A small stress can change the antiferrodistortive transition temperature. Also, the presence of defects can change the occupation of the different inequivalent sites. All these factors make it impossible to predict precisely the intensities of the replica which, as discussed, can change from sample to sample.

IV. CONCLUSION

In this paper, we have presented high-resolution measurements of the infrared absorption of the O-H dipole in SrTiO_3 . It has been shown that infrared spectroscopy of this impurity is a very sensitive probe for the microscopic structure and its dynamics. In particular, we have used this technique to investigate the structural phase transition and the ferroelectric fluctuations. Also, we have made use of the results of infrared measurements to assign a position to the hydrogen atoms in the perovskite structure. This position is found to be on the faces of the cubic cell, between Sr and O atoms. High-energy replicas of the main absorption peaks have been assigned to the effect of ferroelectric fluctuations on the microscopic environment of the dipole. High-resolution infrared investigation of other perovskites (or of alloys that can vary the intensity of the ferroelectric fluctuations) would result in more information and would help in confirming our model.

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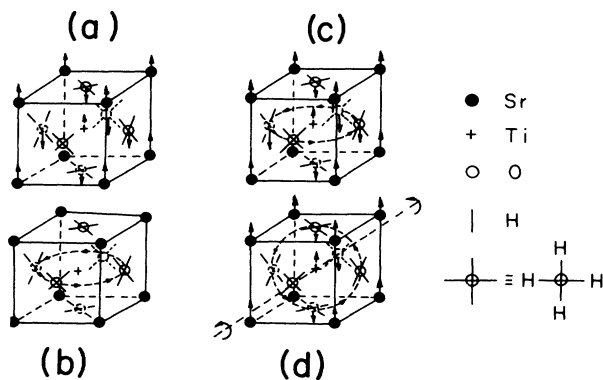


FIG. 5. Atomic displacement associated with (a) the zone center ferroelectric phonon, (b) the zone corner antiferrodistortive phonon, (c) the combination of (a) and (b) with the axes parallel, (d) with the axes perpendicular.

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