In spite of these objections, I feel these papers have made a contribution the great importance of which should be more widely recognized.

I would like to acknowledge stimulating and useful discussions with E. I. Blount, R. G. Shulman, and M. H. Cohen.

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SOFT PHONON MODES AND THE 110°K PHASE TRANSITION IN $SrTiO_3$

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We propose a new interpretation of the 110°K phase transition in $SrTiO_3$, in which the essential feature is a soft phonon at the corner of the cubic Brillouin zone. This interpretation is supported by new evidence from the temperature-dependent Raman spectrum as well as by results of earlier experiments and calculations. Several other experimental results are explained or predicted on the basis of our model for the phase transition.

Strontium titanate is known to undergo a nonferroelectric phase transition at $T_0 = 110$°K from a cubic perovskite to a tetragonal structure.[1,2] Yet the detailed nature of the phase transition has remained unclear. Associated with the phase transition are striking changes in the sound velocity,[3-5] the Rayleigh[4] and Raman[5,6] spectra, and the ESR.[2,7] In this Letter we propose a microscopic model for the 110°K phase transition which provides a basis for understanding the above experiments[3-7] and which is supported by new evidence from the temperature-dependent Raman spectrum. Our interpretation is motivated largely by the low-temperature structure (D_{4h}^{18}) of $SrTiO_3$ suggested in the recent ESR work by Unoki and Sakudo,[7] and is fundamentally different from the interpretation of Cowley.[8] The basic features of our model are (a) that as $T \to T_0$ from above, the triply degenerate phonon F_{2u} (Γ_{25}) at the R point of the Brillouin zone softens (approaches zero frequency); (b) for $T \leq T_0$ the point R is then a reciprocal lattice point so that the unit cell is twice as large as in the cubic phase and the number of zone-center excitations is doubled; (c) as T is lowered from T_0, the two new zone-center phonons, whose progenitor was the F_{2u} zone-corner phonon, increase in frequency or "harden."

Our experimental evidence for these conclusions consists of (1) the appearance of several sharp lines in the Raman spectrum below 110°K, (2) a definite softening of two of these phonon frequencies as $T \to T_0$ from below (see Fig. 1), and (3) the direct interaction of these two phonons with components of the "ferroelectric" mode, observed using the technique of electric-field-induced Raman scattering[9] (EFIRS) and by tuning the "ferroelectric" mode frequencies with an electric field.[10]

The experimental apparatus is as described elsewhere.[10,11] The intrinsic (no external electric field) Raman spectra for various temperatures have been presented elsewhere and need not be reproduced here.[6,11-14] Above 110°K the spectrum consists of several broad bands which have been interpreted, we believe correctly, by Nilsen and Skinner[6] as entirely due to second-order scattering. Below 110°K five additional sharp lines appear at 15, 48, 146, 235, and 460 cm^{-1}. (These are the frequencies at 15°K.) While most of the features have been noticed by other workers,[6,12-14] they have always been, in

our view, misinterpreted. Previous interpretations range from strain-induced and shifted versions of the infrared (IR) modes[12,13] ("ferroelectric" and other TO's at 170 and 560 cm^{-1}) to local modes induced by impurities.[6] Our earlier work with EFIRS has shown clearly the presence of the IR modes at their accepted frequencies,[10,11] none of which exhibits noticeable change at 110°K.

We interpret these sharp lines in the Raman spectrum as scattering from the additional zone-center phonons, resulting from the doubled unit cell. They are made Raman active by the B_{2u} distortion accompanying the slight rotation of the oxygen octahedra in the (001) plane.[7] The Raman tensor components predicted by our model are listed in Table I and compared with our experimental observations. Column I lists the irreducible representations of the R-point phonons in the cubic phase. Their approximate frequencies based on Cowley's calculations[8] from neutron-scattering data in the [100] direction appear in column II. The irreducible representations of the zone-center phonons below 110°K are listed in column III. These are the symmetries at zone center resulting from the distortion at 110°K acting on the corresponding phonons listed in column I. Column IV lists the IR or Raman activity and the Raman tensors predicted by the model. In columns V and VI we list the observed frequencies and Raman tensor elements. Columns V and VI are to be compared with columns II and IV, respectively. The agreement between observations and the predictions of the model is excellent. Because of domain structure[1] the tetragonal axis of the crystal has no unique direction in the laboratory. Therefore, we can distinguish only between diagonal and off-diagonal elements in the Raman tensor. Appreciable off-diagonal elements were observed unambiguously only for the 143-cm^{-1} line (E_g) and the 15-cm^{-1} line (E_g). The E_g component at 460 cm^{-1} was not observed. Also the 235-cm^{-1} feature can only tentatively be identified as first order because this peak sits just at the top of a large second-order peak and the sharp component exhibits diagonal scattering in contrast to the model predictions.

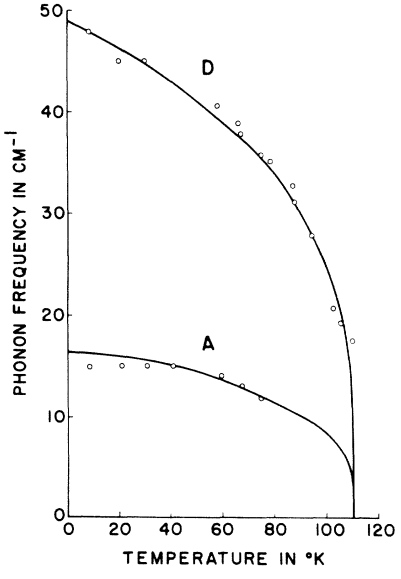

FIG. 1. Temperature dependence of the soft-phonon modes in the tetragonal phase. Smooth curves are of the form $\omega = \text{const} \times (T_0 - T)^n$ with $T_0 = 110°K$; $n = 0.31$. Data can be fit with $n = 0.31 \pm 0.03$.

Since the two lowest-frequency Raman-active modes (designated A and D in our previous work) originate from the soft, triply degenerate F_{2u} (Γ_{25}) mode in the cubic phase, one might expect the frequencies of both A and D to soften as $T - T_0$ in the tetragonal phase. This behavior is clearly shown in Fig. 1. The solid lines describe a temperature dependence of the form $\omega = \text{const} \times (T_0 - T)^n$, where $T_0 = 110°K$ and $n = 0.31$. This is

Table I. Column I, zone-corner phonon characters $(\frac{1}{2},\frac{1}{2},\frac{1}{2})\pi/a$. Column II, zone-corner phonon frequencies in cm^{-1} estimated by Cowley (Ref. 8). Column III, zone-center symmetries below 110°. Column IV, Raman tensor elements predicted. Column V, Raman frequencies observed, in cm^{-1}. Column VI, Raman tensor symmetries observed: D for diagonal elements, N for nondiagonal.

Cubic		Tetragonal			
I	II	III	IV	V	VI
$A_{2u}(\Gamma_2')$	~800	A_{2g}	Silent	···	···
$F_{2g}(\Gamma_{25}')$	~500	E_u	IR	···	···
		A_{1u}	Silent	···	···
$F_{1u}(\Gamma_{15})$	~400	E_g	xz,yz	460	D
		B_{1g}	$xx,-yy$		
$E_u(\Gamma_{12}')$	200-300	B_{2g}	xy	235	$N,D(?)$
		A_{2g}	Silent		
$F_{1u}(\Gamma_{15})$	~110	E_g	xx,yz	143	N,D
		B_{1g}	$xx,-yy$		
$F_{2u}(\Gamma_{25})$	Soft	E_g	xz,yz	15[a]	N
		A_{1g}	xx,yy,zz	48[b]	D

[a]Line designated as A.
[b]Line designated as D.

only a suggested form. There is no a priori requirement that both ω_A and ω_D exhibit the same form of temperature dependence; nor is it necessary that their frequencies precisely vanish at T_0.

Further confirmation of the identification of A and D as zero-wave-vector phonons and of their symmetry assignments is provided in Fig. 2, where the interactions of modes A and D with the components "ferroelectric" mode (B and C) are illustrated. The data here were obtained as in Ref. 10 on EFIRS and merely extended over a wider range of electric fields. In the presence of an external electric field the crystal symmetry is further reduced (inducing Raman activity in the "ferroelectric" mode): to C_{4v} if E is parallel to the tetragonal axis, and to C_{2v} if E is perpendicular. In either case modes A and B then have the same symmetry and are therefore expected to exhibit an "anticrossing" as ω_B is tuned with the electric field[10] through ω_A. A similar "anticrossing" is expected for modes C and D since they are of the same symmetry. Notice that in Fig. 2 the interactions are clearly visible, at 1.5 kV/cm for A and B, and at 15 kV/cm for C and D. Notice also that ω_C passes freely through ω_A at 1.3 kV/cm, as expected. Since equality of wave vectors, as well as symmetry and frequency, is necessary for such interactions, the observation of these interactions is evidence that both A and D are zone-center phonons.

The implications of our model for experiments other than Raman scattering will now be briefly discussed. Of these one of the most interesting is the sound-velocity behavior near 110°K. Experimentally,[3-5] both the longitudinal and transverse sound velocities remain fairly constant as T is decreased toward 110°K. Within about a one-degree interval of 110°K all the velocities decrease suddenly by several percent. Below 110°K the temperature dependence differs for differing acoustic branches, but is generally less severe than immediately above 110°K. Cowley[8] has associated the temperature dependence of the sound velocity with that of the "ferroelectric" phonon by means of three-phonon interactions. Our suggestion is essentially different: Above 110°K the relevant soft mode is at the zone corner and no interaction with the zone-center acoustic phonons is operative. As 110°K is reached the soft optic phonon mode appears at zone center, where it interacts with the acoustic phonon—depressing its frequency. As T is lowered from 110°K the optic-phonon frequency increases, relieving the pressure on the acoustic branch and allowing the sound velocity to increase gradually. However, it is not possible for us to say definitely whether the interaction which lowers the sound velocity is harmonic, taking place in the tetragonal phase, as described above, or anharmonic in the cubic phase. The distinction is somewhat academic since the allowed harmonic interactions in the tetragonal phase can be viewed as anharmonic interactions involving the frozen zero-frequency distortion of the B_{2u} phonon at the zone corner. More detailed work is necessary to make quantitative the relation between the optic and acoustic phonon and their temperature dependences, but this model should provide a good basis for such work.

Our model predicts new experimental effects in several as yet untested areas. First, a new IR-active mode (E_u) is predicted below 110°K. Because the angle of rotation of the oxygen octahedron increases as T is lowered,[7] we expect the IR oscillator strength to increase as T is lowered. We suggest that the low-temperature IR spectrum of $SrTiO_3$ be examined with particular attention paid to the 500-cm^{-1} region (see Table I). Second, inelastic neutron scattering experiments in the vicinity of the R point of the Brillouin zone should be undertaken (1) to measure the frequencies of the modes listed in column I of the table for comparison of the Raman frequencies of column V, and (2) to observe the

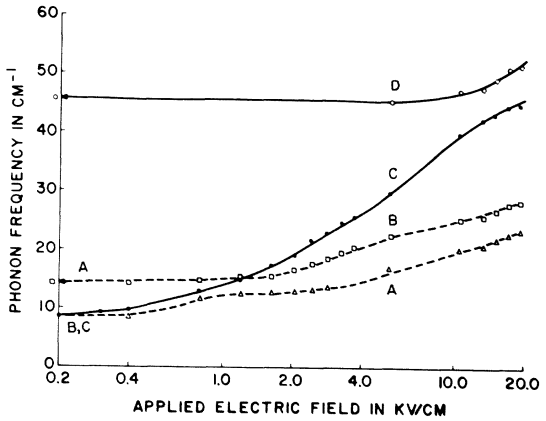

FIG. 2. Electric field dependence of four low-frequency phonons in $SrTiO_3$ at 10°K; illustrating the interactions between modes of E_g symmetry (dashed lines) and between modes of A_{1g} symmetry (solid lines). The modes labeled B and C are components of the IR-active "ferroelectric" mode discussed in Ref. 10. The left-directed arrows on the curves for A and D indicate frequencies measured at zero field.

behavior of the F_{2u} (Γ_{25}) mode as a function of temperature. We believe that the predicted phonon behavior will be more readily observed by studying phonons at the R point, rather than the Γ point. [Note added in proof.—Neutron scattering in the vicinity of the R point is currently being studied by G. Shirane and Y. Yamada. Their preliminary results confirm the predictions of our model. We are grateful to these authors for communicating their results prior to publication.] Third, the effects of phonons on the semiconducting and superconducting[15] properties of doped $SrTiO_3$ should be re-examined, especially in view of the presence of additional soft-phonon modes in the tetragonal phase. Finally any crystal properties associated with band structure, such as optical absorption in the uv, should be affected by the halving of the Brillouin zone at 110°K. For example, we expect that the indirect band gap, as calculated by Kahn and Leyendecker[16] in the cubic phase, should become direct below 110°K.

We are grateful to D. C. O'Shea for freely discussing his work on $SrTiO_3$, for providing us with a copy of his thesis, and in particular, for pointing out the temperature dependence of modes A and D. We also thank L. E. Cheesman for technical assistance, W. Pleibel for crystal polishing, and T. W. Armstrong, Jr., for electrode evaporation.

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EPR OF ATOMS AND RADICALS IN RADIATION-DAMAGED SOLID H_2 AND HD*

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Paramagnetic resonance of electronic states of atoms and radicals trapped in solid H_2 and HD at 4.2°K after 4×10^6 R of radiation damage have been investigated at 24 GHz. The apparent spin-lattice relaxation time of resonances of H atoms is damaged solid HD formed from gas containing 3×10^{-4} O_2 was found to be 0.14 msec at 4.2°K and approximately 0.27 msec at 1.2°K. Furthermore, these H atoms in solid HD remained stably trapped at 4.2°K for periods in excess of two months.

Paramagnetic resonance of electronic states of atoms and radicals trapped in solid H_2, HD, and D_2 at liquid-helium temperatures has particular interest because dynamically oriented nuclei in HD and D_2 would constitute polarized targets useful for the study of elementary particles. In previous experiments[1,2] with trapped atoms produced by radiation damage of these solids, relaxation times for the paramagnetic transitions were too long to permit effective dynamic orientation. We have investigated the spectrum for EPR at 24 GHz of radiation-damaged solid H_2 and HD prepared both from relatively pure gases and from gases containing several parts in 10^4 impurity of O_2, and have observed substantial reduction of the apparent spin-lattice relaxation time of reso-