Soft acoustic mode in ferroelastic $BiVO_4$

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(Received 2 July 1981)

Brillouin scattering spectroscopy of bismuth vanadate has revealed a soft acoustic mode which is characteristic of a proper ferroelastic phase transition. Raman scattering has revealed an optic mode which is doubly degenerate E_g in the paraelastic phase and splits into two B_g modes in the ferroelastic phase. The temperature dependence of the splitting is also consistent with a proper ferroelastic transition.

Since Bierlein and Sleight[1] discovered the ferroelastic phase transition in bismuth vanadate at $T_0 = 528$ K, extensive x-ray and neutron-diffraction studies have supported their interpretation of the tetragonal $4/m$ to monoclinic $2/m$ transition as a proper ferroelastic transition with paraelastic and ferroelastic space groups $C_{4h}^6(I4_1/a)$ and $C_{2h}^6(I2/b)$, respectively.[2,3] Furthermore, Raman scattering experiments by Pinczuk *et al.*[4–6] revealed a temperature-dependent low-frequency zone-center optic mode with B_g symmetry in the $4/m$ paraelastic phase and A_g symmetry in the $2/m$ ferroelastic phase, consistent with the requirement of group theory for the soft mode driving this transition.[7] It has therefore been generally accepted that the transition is driven by a B_g zone-center soft-optic mode which in turn forces the frequency of a soft-acoustic mode to which it is linearly coupled to zero at T_0, triggering the transition.

There are, however, three causes of concern in accepting this interpretation:

(1) The amount of softening of the "soft"-optic mode is rather small, and its frequency extrapolates to zero more than 200 K below T_0.[5] Furthermore, the Raman spectrum of $LaNbO_4$ (which is isostructural to $BiVO_4$ and exhibits a similar ferroelastic transition) shows no temperature dependence for the frequency of the equivalent B_g mode above T_0.[8]

(2) Dudnik *et al.* have concluded that the $BiVO_4$ transition is cell doubling ($I4_1/c \rightarrow P2_1/c$) which would make it an *improper* ferroelastic transition.[9] We note that the paraelastic phase has the body-centered tetragonal scheelite structure in all analyses; the difference in structure assignments occurs in the ferroelastic phase where the unit-cell volume would double if the VO_4 group at the center of the unit cell is slightly rotated or translated relative to (and therefore no longer equivalent to) the VO_4 groups at the cell corners, a distinction which is very difficult to establish by structural analysis alone.

(3) Finally, while the proper ferroelastic transition model implies an elastic instability at T_0 with complete softening of a B_g acoustic mode,[5] no soft acoustic mode has ever been reported.

In this Communication we report the observation by Brillouin scattering of a soft acoustic mode in $BiVO_4$, and of the temperature-dependent splitting of a pair of B_g optic modes in the Raman spectrum in the ferroelastic phase which arise from a doubly degenerate E_g mode in the paraelastic phase. We believe that these observations conclusively demonstrate the correctness of the proper ferroelastic interpretation of this transition.

BRILLOUIN SCATTERING

A rectangular sample approximately $3 \times 6 \times 7$ mm^3 with two c faces and the remaining faces oriented at approximately 45° to domain walls was cut from one of several large single crystals generously provided by Dr. A. W. Sleight of the Central Research and Development Department, E. I. duPont de Nemours and Company.[2] X-ray Laue photographs indicated that at room temperature the domain walls are oriented at approximately 30° to the pseudotetragonal axes. This agrees reasonably well with the 36° orientation predicted by Sapriel's tables,[10] using the monoclinic strains indicated by Fig. 5 of David, Glazer, and Hewat.[3]

Right-angle Brillouin scattering in the xy plane was excited by a krypton ion laser at 6471 Å and analyzed with a piezoelectrically scanned Fabry-Perot interferometer. (The Brillouin scattering apparatus and the sample oven are described in a recent article by Yao, Cummins, and Bruce.[11]) A typical set of Brillouin spectra in VV polarization for $T < T_0$ is shown in Fig. 1.

With the scattering vector $\vec{q}$ perpendicular to one set of domain walls, the Brillouin shift of the in-plane transverse mode decreased from ~ 0.4 cm^{-1} at room temperature to about 0.1 cm^{-1} at T_0 and then increased as $(T - T_0)^{1/2}$ up to 570 K, the maximum temperature investigated (see Fig. 2).

In the ferroelastic phase the Brillouin components

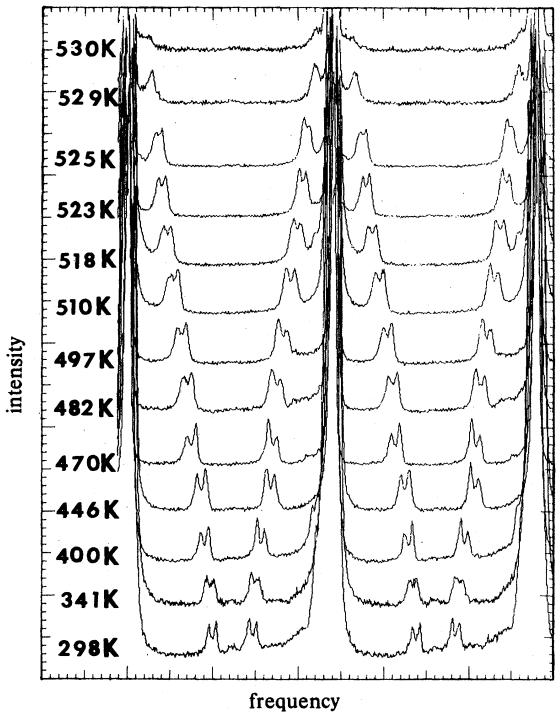

FIG. 1. Brillouin scattering spectra of $BiVO_4$ at various temperatures in the ferroelastic phase with VV polarization. The free spectral range is 0.92 cm^{-1}. The splitting of the Brillouin components is associated with the presence of domains as discussed in the text.

observed in VV polarization are split, presumably due to the relative rotation by several degrees of the optical indicatrices in the two types of domains due to the spontaneous piezo-optic effect.[9] We also observed that the transmitted beam emerged from the sample as two slightly divergent beams for $T < T_0$, but as a single beam for $T > T_0$ when the domain walls are absent.

Standard analysis of the Brillouin scattering tensors predicts Brillouin activity for this mode only for HH polarization in the paraelastic phase, but for both HH and VV polarizations in the ferroelastic phase, consistent with our observations. The analysis also predicts that the angle ϕ between the direction of propagation of the soft acoustic mode and the tetragonal axes is given by $\tan(4\phi) = 4C_{16}/(C_{11} - C_{12} - 2C_{66})$, and that the velocity v of the soft acoustic mode is determined by

$$\rho v^2 = \tfrac{1}{4}\{C_{11} - C_{12} + 2C_{66} - [(C_{11} - C_{12} - 2C_{66})^2 + 16C_{16}^2]^{1/2}\} \quad . \qquad (1)$$

We note that the stability condition based on the vanishing of an eigenvalue of the 6×6 elastic constant tensor predicts that the transition occurs when the critical constant C_c reaches zero, where[12]

$$C_c = \tfrac{1}{2}\{C_{11} - C_{12} + C_{66} - [(C_{11} - C_{12} - C_{66})^2 + 8C_{16}^2]^{1/2}\} \quad , \qquad (2)$$

although ρv^2 of Eq. (1) and C_c of Eq. (2) vanish simultaneously, they are not generally equal.

The failure of the observed soft-acoustic-mode frequency to reach zero at the transition may be due either to slight misalignment of the sample or to the transition being slightly first order. But its temperature dependence is entirely inconsistent with a zone-boundary instability-driven improper ferroelastic transition where the acoustic anomaly would be weak and extremely asymmetric. The distinction is immediately apparent in comparing our results with the results of Rehwald and Vonlanthen for squaric acid, a crystal which also undergoes a $4/m$ to $2/m$ transition, but with a doubling of the volume of the unit cell.[13]

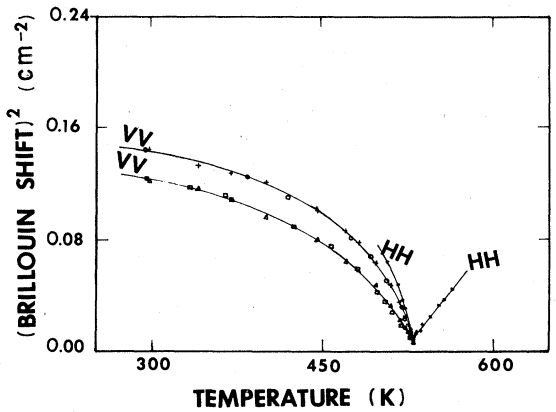

FIG. 2. Observed Brillouin shifts for the soft acoustic mode as a function of temperature. Different symbols represent different experimental runs.

RAMAN SCATTERING

Raman spectra were obtained in both right-angle and backscattering geometries with krypton ion-laser excitation at 6471 Å and a conventional Spex tandem spectrometer. Digital spectra were stored in a computer for subsequent nonlinear least-squares lineshape analysis. The low-frequency Raman spectra were in substantial agreement with those reported by Pinczuk, Burns, and Dacol, and gave similar soft-mode parameters.[4,5] We also investigated several higher frequency modes, particularly a mode at 120 cm^{-1} which is E_g in the tetragonal phase and splits into two well resolved B_g modes in the monoclinic phase. A similar splitting of an E_g mode in $LaNbO_4$ was observed by Wada *et al.*[8] The frequencies ω_1 and ω_2 deduced from a two-damped oscillator fit to backscattering Raman spectra are shown in Fig. 3.

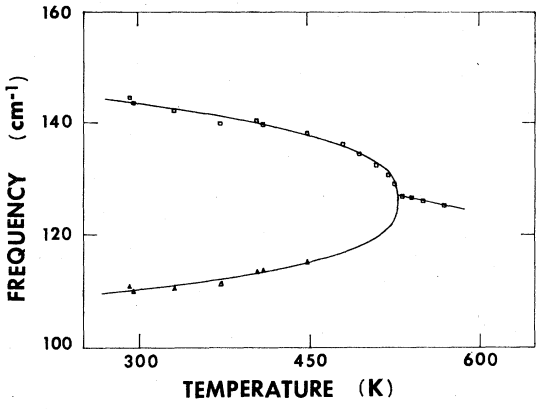

FIG. 3. Frequencies of the doubly degenerate tetragonal E_g mode and the two corresponding monoclinic B_g modes from computer fits to Raman backscattering data.

A power-law fit of $\omega_2^2-\omega_1^2$ against T_0-T gave

$$\omega_2^2-\omega_1^2 \cong 1186(T_0-T)^{0.36} \ . \tag{3}$$

If the transition is driven by a zone-center optic mode with coordinate Q, transforming according to the B_g representation of the group $4/m$, then the potential energy of the E_g mode including the lowest-order anharmonic coupling to Q is of the form

$$V=\tfrac{1}{2}M_E\omega_E^2(e_1^2+e_2^2)+\tfrac{1}{2}a(e_1^2-e_2^2)Q+be_1e_2Q \ , \tag{4}$$

where e_1 and e_2 are the coordinates of the E_g mode, M_E its effective mass, and ω_E its unperturbed frequency. Below the transition, we can approximate Q in the last two terms by its nonzero average value η. Diagonalizing the resulting potential energy, we get two modes with frequencies

$$\omega_{1,2}^2=\omega_E^2\pm\eta(a^2+b^2)^{1/2} \ . \tag{5}$$

Therefore, $\omega_2^2-\omega_1^2$ would increase linearly with the order parameter. On the other hand, if the transition is driven by a (two-dimensional) zone-boundary mode with coordinates q_1 and q_2, then the coupling terms are of the form $(e_1^2-e_2^2)(q_1^2+q_2^2)$ and $e_1e_2(q_1^2+q_2^2)$, from which it follows that $\omega_2^2-\omega_1^2$ would increase as the square of the order parameter η^2. Our result is consistent with a zone-center transition, and would yield an exponent β closer to 0.5 if the transition is slightly first order, but is again inconsistent with a zone-boundary transition.

In conlcusion, we believe that the temperature dependence of the soft acoustic mode observed in our Brillouin scattering experiments, together with the temperature-dependent splitting of the doubly degenerate optic mode observed in Raman scattering, firmly establish the $BiVO_4$ transition as a proper ferroelastic phase transition.

ACKNOWLEDGMENTS

We are greatly indebted to A. W. Sleight and G. Burns for generously providing samples of bismuth vanadate, to R. Callender for the loan of a krypton ion laser, to J. Wicksted and M. Matsushita for help in the Raman scattering experiments, and to A. Pinczuk for helpful discussions. This work was supported by the National Science Foundation under Grant No. DMR 8020835 and by the PSC-BHE Research Award Program of CUNY.

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