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## Elastic Anomaly and Phase Transition of BaTiO<sub>3</sub>

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The acoustic-phonon velocities of a single crystal of BaTiO<sub>3</sub> have been measured as a function of pressure up to 8 GPa, including the transition pressure  $p_c = 2.35$  GPa, by means of Brillouin scattering technique. Only one elastic eigenmode shows an anomalous decrease on approaching  $p_c$  and the elastic anisotropy increases. The elastic anomaly of cubic BaTiO<sub>3</sub> is interpreted well by introducing a new tensorial order parameter which describes the anisotropy. The cubic-to-tetragonal phase transition in BaTiO<sub>3</sub> is shown to be triggered by the fluctuation of the anisotropy, not the polarization itself.

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Studies on the cubic-to-tetragonal phase transition in BaTiO<sub>3</sub> have been extensively done,<sup>1,2</sup> using a variety of experimental methods. The result of an infrared measurement by Luspín, Servoin, and Gervais showed that the frequency  $\omega_s$  of the soft phonon mode varies from 1350 to 520 K as  $\omega_s^2 \propto T - T_c$ , but becomes independent of temperature below 520 K to  $T_c$ ,<sup>3</sup> and suggested the existence of a crossover from displacive to order-disorder type of transition.<sup>4</sup> The recent results of hyper-Raman-scattering measurements, which were done independently by Inoue and Akimoto<sup>5</sup> and by Vogt, Sanjurju, and Rossbroich,<sup>6</sup> were in conflict with each other as to the interpretation of the phase transition, i.e., whether the mechanism of the phase transition is of the order-disorder type or of the displacive type. Thus the controversy on the mechanism of the phase transition is still unresolved.

A measurement of inelastic neutron scattering showed the existence of a strong anisotropy in the spectra near the phase transition.<sup>7</sup> The anisotropy seems to be related to the elastic anisotropy. Although the elastic anomaly of BaTiO<sub>3</sub> was observed in the cubic phase near the phase transition,<sup>8</sup> the contribution of the elastic anisotropy to the phase transition was not elucidated since the experiments on the elastic properties were partly performed within the limited region close to the phase transition. Thus no systematic study of the elastic properties of BaTiO<sub>3</sub> has been hitherto performed in relation to the elastic anisotropy. If the anisotropy plays an important role in the phase transition, the studies on the elastic properties will give important information on the mechanism of the phase transition since the anisotropic fluctuation should be of relaxational type.

By means of the Brillouin scattering technique in combination with a diamond anvil cell, we have performed the first systematic study of the elastic properties of BaTiO<sub>3</sub> for a wide region including the phase-transition point, as a function of pressure at room temperature. We have found that the elastic anisotropy increases anomalously on approaching the phase transition. The purpose of this paper is to give new insight into the

phase-transition mechanism of BaTiO<sub>3</sub> on the basis of the elastic anomaly accompanying the phase transition.

The *b*-cut plates were prepared from a melt-grown BaTiO<sub>3</sub> single crystal (NEC Co. Ltd.) which has the transition temperature 127°C at normal pressure. The sample used was typically 20×200×200 μm<sup>3</sup> in size and was set in a diamond anvil cell. The high-pressure Brillouin scattering measurements were performed with use of a five-pass Fabry-Perot interferometer (Burleigh DAS-1 system) and a Kr-ion laser with wavelength of  $\lambda = 647.1$  nm and power of 140 mW. A 90° scattering geometry was used, so that the laser beam was incident at 45° to the sample plate and the scattered light was collected at 90° with respect to the laser beam. The acoustic-phonon velocities were measured for the case of the wave vector  $\mathbf{q}$  parallel to [100], [001], and [101]. The polarization of the incident radiation was parallel to the scattering plane and no analyzer was used. In the present geometry the Brillouin frequency shift  $\Delta\nu$  is related to the acoustic velocity  $v$  by the expression

$$v = \lambda \Delta\nu / \sqrt{2}, \quad (1)$$

which is independent of the refractive index of the sample.<sup>9,10</sup> All measurements were performed at room temperature, 23°C.

The pressure dependence of the acoustic-phonon velocities is shown in Fig. 1. It is clear that the acoustic velocities change linearly with pressure in the tetragonal phase up to the transition pressure  $p_c = 2.35$  GPa. In the cubic phase, however, a large deviation from the linear pressure dependence of the velocities is observed over a wide pressure range near the transition pressure. Although we are concerned with the anomaly of the velocity in the cubic phase, it should be pointed out that the mode (1') showing the strongest pressure dependence in the tetragonal phase, which is called the coupled mode,<sup>10</sup> is related to spontaneous polarization.

In a similar manner as done for SrTiO<sub>3</sub>,<sup>9</sup> the density as a function of pressure can be determined from the acoustic velocities in the cubic phase as follows:

$$\rho = \rho_0 + (p \times 10^3) / (23.13 + 0.5338p), \quad (2)$$

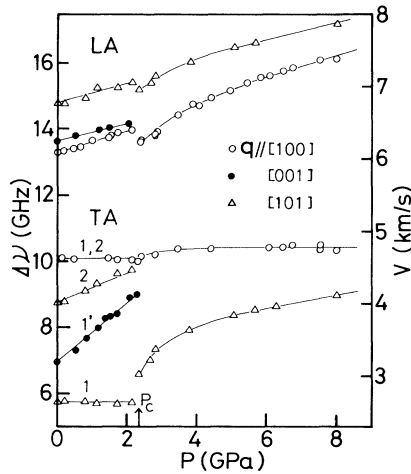


FIG. 1. The Brillouin frequency shifts or the acoustic-phonon velocities vs pressure. In the tetragonal phase the numbers 1 and 2 imply two nondegenerate TA modes for  $q\parallel[100]$  and  $[101]$ , respectively, and the primed number 1' the degenerate one for  $q\parallel[001]$ . For  $q\parallel[100]$  the splitting of TA modes was very small, and the scattering intensity of both TA modes was too weak to observe the splitting clearly. The mode assignments in the tetragonal phase were confirmed by measuring the dependence of the velocities on the propagation direction at normal pressure (Ref. 10).

where  $\rho$  and  $p$  are described in units of  $\text{kg/m}^3$  and GPa, respectively, and  $\rho_0 = 6.03 \times 10^3 \text{ kg/m}^3$  is the density of cubic  $\text{BaTiO}_3$  at room temperature obtained by extrapolation from the high-temperature cubic phase. In the calculation of Eq. (2) we assumed that the ratio of the specific heats at constant pressure and volume,  $C_p/C_v$ , is equal to 1. From Eq. (2) the bulk modulus  $B_t(p=0) = 139.4 \text{ GPa}$  and the pressure derivative  $B_t'(p=0) = 7.44$  are obtained. The elastic stiffness constants are evaluated from the observed acoustic velocities with use of Eq. (2) and are shown in Fig. 2 for three elastic eigenmodes  $C_A$ ,  $C_E$ , and  $C_T$ , where  $C_A = (C_{11} + 2C_{12})/3$ ,  $C_E = (C_{11} - C_{12})/2$ , and  $C_T = C_{44}$ . While both  $C_A$  and  $C_T$  change linearly with pressure,  $C_E$  decreases anomalously from the linear part over a pressure range of about 3 GPa above the transition pressure  $p_c$ . The linear part of the pressure dependence of the elastic constants may be determined from the data in the high-pressure region sufficiently far from the transition pressure.

The elastic anisotropy which is defined by  $\eta = (C_T - C_E)/C_E$  increases in going toward  $p_c$  from high pressure as shown in Fig. 3. Note that the behavior of  $\eta$  is analogous to those of the dielectric constant<sup>1</sup> and the spectral intensity of the inelastic neutron scattering,<sup>7</sup> which exhibit a strong anisotropy. Thus it is clear that an anisotropic field plays an important role in the phase transition of  $\text{BaTiO}_3$ . Therefore, in addition to the polarization, we introduce a new order parameter  $S$  which describes the anisotropic field.

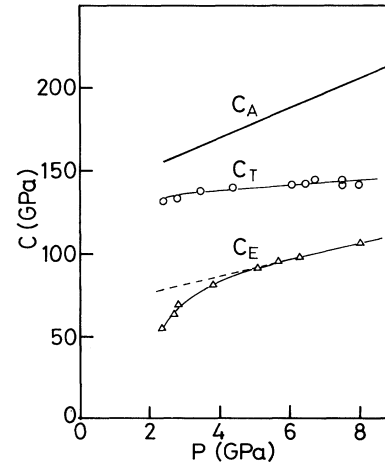


FIG. 2. The pressure dependence of the elastic eigenmodes in the cubic phase of  $\text{BaTiO}_3$ , where  $C_A = (C_{11} + 2C_{12})/3$ ,  $C_E = (C_{11} - C_{12})/2$ , and  $C_T = C_{44}$ . The values of  $C_A$  were evaluated from the observed values of  $C_{11}$  and  $C_E$ .

The anisotropic field may be described with a symmetric traceless second-rank tensor having quadrupole symmetry. It should be emphasized that the newly introduced anisotropy tensorial order parameter is not an acoustic property but is composed of local displacements involving charge redistribution, and it is this tensorial fluctuation which drives the acoustic instability. If a local ordered state were considered as a dynamic cluster, it would cause the anisotropic field. Thus the anisotropy  $S$  may be interpreted in terms of the dynamic cluster. To our knowledge such a tensorial order parameter has never been considered in the treatment of the ferroelectric phase transition while the tensorial order parameter is familiar in the field of liquid crystals.<sup>11</sup> Further, it should also be noted that a coupling of the acoustic pho-

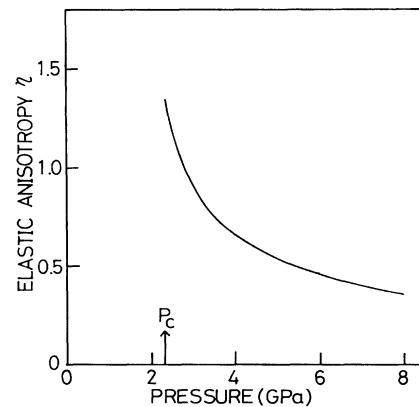


FIG. 3. The elastic anisotropy  $\eta$  vs pressure, where  $\eta = (C_T - C_E)/C_E$ .

non to the anisotropy of the polarizability was found in a plastic crystal.<sup>12</sup>

The symmetric traceless second-rank tensor reduces to parts associated with the irreducible representations  $E_g$  and  $T_{2g}$  under the point group symmetry  $O_h$  to which  $\text{BaTiO}_3$  belongs. If we take into account the fact that only the  $C_E$  mode shows an anomaly, the  $E_g$  part of  $S$  is taken as the order parameter. With the assumption that the principal axis of the tensor is along the crystalline axis, the tensor components may be, in general, represented as  $S_{xx} = -(Q+R)/2$ ,  $S_{yy} = -(Q-R)/2$ , and  $S_{zz} = Q$ , where  $Q$  and  $R$  are parameters related to the anisotropy. The  $E_g$  parts of  $S$ ,  $S_{E1}$  and  $S_{E2}$ , which are equal to  $R$  and  $\sqrt{3}Q$  couple to the strain components  $x_{E1} = x_1 - x_2$  and  $x_{E2} = (2x_3 - x_1 - x_2)/\sqrt{3}$ , respectively.

In  $\text{BaTiO}_3$  the effect of pressure and temperature on the phase transition seems to be equivalent since the pressure dependence of the dielectric constant is expressed in the form of  $C/(p-p_c)$ , analogous to the Curie-Weiss law, and the pressure dependence of the Curie constant is negligibly small.<sup>13</sup> Therefore, in the following discussion of the phase transition the temperature and pressure are treated as the equivalent thermodynamic variable. The free energy may be represented in terms of the polarization  $P$ , the anisotropy  $S$ , and the strain  $x$  as follows:

$$F = F(P) + F(S) + F(x) + F(P, x) + F(S, x) + F(P, S), \quad (3)$$

$$F(P) = \frac{1}{2} K_1 \sum P_i^2 + A \left[ \sum P^2 \right]^2 + A_n \sum (P_i P_j)^2 + B \sum P_i^6, \quad (4)$$

$$F(S) = \frac{1}{2} K_2 (S_{E1}^2 + S_{E2}^2), \quad (5)$$

$$F(x) = \frac{1}{2} \sum C_{ij} x_i x_j, \quad (6)$$

$$F(P, x) = \sum q_{ijk} x_i P_j P_k, \quad (7)$$

$$F(S, x) = (g_{11} - g_{12}) (S_{E1} x_{E1} + S_{E2} x_{E2}), \quad (8)$$

$$F(P, S) = (h_{11} - h_{12}) [S_{E1} (P_1^2 - P_2^2) + S_{E2} (2P_3^2 - P_1^2 - P_2^2)/\sqrt{3}], \quad (9)$$

where only the lowest order of the power of  $S$  is considered since  $S$  is of order  $P^2$ . It is assumed that the  $K_1$  and  $K_2$  alone are temperature dependent;  $K_1 = (T - T_1)/a_1$  and  $K_2 = (T - T_2)/a_2$ , where  $a_1$  and  $a_2$  are constants. The phase transition may take place at  $K_1 = 0$  or  $K_2 = 0$  according to whether the divergence of the fluctuation is caused by the polarization or the anisotropy, except for an accidental degeneracy.

The electrostrictive coupling term  $F(P, x)$  contributes to the discontinuous jump of the elastic constants just at the phase transition but not to the elastic anomaly in the cubic phase.<sup>1,2</sup> Therefore the free energy necessary for analysis may be expressed with the sum of  $F(S)$ ,  $F(x)$ , and  $F(S, x)$  which leads to the dressed elastic constant  $C_E' = C_E - (g_{11} - g_{12})^2 / K_2$ . Then the anomalous part  $\Delta C_E = C_E - C_E'$  will be proportional to the inverse of  $p - p_2$ . The observed behavior of the anomalous part  $\Delta C_E$ , which is obtained by subtracting the observed value of  $C_E$  from the linear part shown with the broken line in

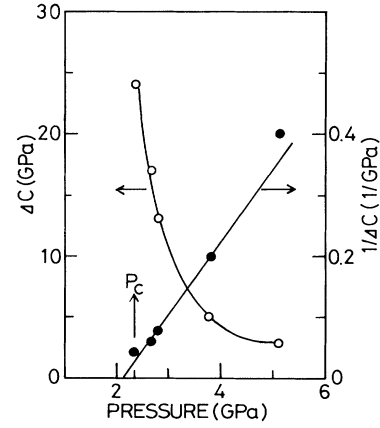


FIG. 4. The anomalous part of the elastic constant  $\Delta C_E$  and the inverse as a function of pressure. The anomalous part is obtained by subtracting the observed value of  $C_E$  from the linear part shown with the broken line in Fig. 2.

Fig. 2, is in agreement with the expected one as shown in Fig. 4. The value of  $p_2$  is determined as  $p_2 = 2.15 \pm 0.05$  GPa, which is very close to the transition pressure  $p_c = 2.35$  GPa. With use of the value of  $dT_c/dp = 44.3$  K/GPa, the temperature difference corresponding to the pressure difference  $p_c - p_2$  is evaluated to be  $8.9 \pm 2.2$  K, in good agreement with the result of the temperature dependence of the dielectric constant.<sup>1</sup> This fact suggests that the phase transition of  $\text{BaTiO}_3$  is triggered by the fluctuation of the anisotropy, which is of relaxational type, but not the polarization. The present result is compatible with the result of a series of EPR studies by Müller and Berlinger<sup>14</sup> which showed that the order-disorder character of  $\text{BaTiO}_3$  is enhanced as a result of the strong anharmonicity of the Ti ion.

The present model shows that the dielectric constant is composed of contributions from the weak temperature-dependent term proportional to  $1/K_1$  and the strong one proportional to  $1/K_2$ . If the coefficient  $a_1$  is much larger

than  $a_2$ , the contribution of the anisotropy should appear in a limited temperature range near the phase transition. This may be the origin of the order-disorder-displacive crossover.<sup>4</sup> The anisotropic fluctuation may cause a strong temperature-dependent Rayleigh and hyper-Rayleigh scattering. The temperature dependence of the hyper-Rayleigh scattering intensity analogous to the dielectric constant was reported by Inoue.<sup>15</sup>

Further, the present model interprets the strong temperature dependence of the coefficient of the fourth power of polarization in the Devonshire theory.<sup>1</sup> The relevant free energy is the sum of  $F(P)$ ,  $F(S)$ , and  $F(P,S)$ . If the free energy were rewritten as a function of the polarization of the coefficients  $A$  and  $A_n$  of  $P^4$  would be modified through the coupling term  $F(P,S)$  to  $A' = A - 2(h_{11} - h_{12})^2/3K_2$  and  $A_n' = A_n + 2(h_{11} - h_{12})^2/K_2$ , respectively, and become strongly temperature dependent. This is the reason why the coefficient of  $P^4$  within the framework of Devonshire theory exhibits an anomalous temperature dependence,<sup>1</sup> which was for a long time puzzling. Note that  $A' < 0$  and  $A_n' > 0$  as the transition point is approached. In that case the phase realized after transition is always the tetragonal one. Thus the phase transition of BaTiO<sub>3</sub> is well understood by introducing the anisotropy order parameter.

An elastic anomaly was also found in CsPbCl<sub>3</sub> (Ref. 16), where the soft mode was highly overdamped. Thus an elastic anomaly accompanied by a phase transition seems to be a common characteristic of crystals of which the soft mode is said to be highly overdamped. As seen from the present model the phase transition of such crystals may also be understood by introducing the anisotropy

order parameter.

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