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Brillouin-Scattering Evidence for a New Phase Transition in Perovskite Crystals: $PrAlO_3$

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Brillouin scattering experiments have revealed a new structural phase transition in $PrAlO_3$ at 118 K, in which strain is the sole order parameter. This fact, together with the second-order nature of the transition, suggests that it belongs to a class of structural transitions first delineated nearly ten years ago by Anderson and Blount.

The cubic perovskite family of solids is well known to be potentially unstable toward structural phase transitions driven by soft phonon modes.[1] Several such purely lattice-dynamical phase transitions have been observed, driven by both Brillouin-zone-center[1] and -zone-boundary soft modes. $PrAlO_3$, for example, undergoes a cubic-rhombohedral transition at 1320 K driven by a soft R-point phonon.[2] In this respect it is similar to $LaAlO_3$ and several other members of the perovskite family.[3] However, because of the interaction between the Pr^{3+} $4f$ electronic levels and the $PrAlO_3$ lattice phonons, two additional structural phase transitions are known to occur as the temperature is lowered: a first-order rhombohedral-orthorhombic transition at 205 K, and a second-order orthorhombic-monoclinic transition at 151 K.[2,4]

We report here a new structural phase transition, of second order, at 118.5 K, which is driven by a soft transverse acoustic phonon. Despite several previous careful studies by a wide variety of techniques (optical absorption[2,5] and fluorescence,[2] neutron[4,6] and Raman scattering,[2] x-ray,[7] ESR,[8] specific heat,[9] and refractive index[10] measurements) this transition has remained heretofore undetected. This fact, together with the extremely large (~99%) acoustic anomaly observed in our Brillouin scattering experiments, strongly suggests that strain is the sole order parameter for this transition. Since the transition is apparently second order and involves a change of crystal symmetry, we suggest that this transition belongs to a class of structural transitions first delineated nearly a decade ago by Anderson and Blount.[11] Furthermore, it lies entirely outside the framework of present theories[2,6] of $PrAlO_3$, its properties, and its phase transitions, which have otherwise proven so successful in imposing order on the multitude of magnetic, structural, and spectroscopic observations in this material.

The sequence of the previously known phase transitions in $PrAlO_3$ can conveniently be viewed in terms of changes in the direction of the axis about which the AlO_6 octahedra rotate in adjacent cubic unit cells.[2,6] Between 1320 and 210 K this axis is along ⟨111⟩. Between 210 and 151 K, it is ⟨101⟩. Below 151 K it begins to rotate, and continuously approaches ⟨001⟩ as the temperature

approaches absolute zero. Both of these transitions arise from strong interactions between the Pr^{3+} electronic states (excitons) and the perovskite lattice modes (phonons), with the result that virtually *all* of the experiments cited in the previous paragraph can couple rather directly to the order parameter. Indeed, the $PrAlO_3$ 151-K transition is probably the most completely studied structural phase transition from the viewpoint of direct order-parameter measurements.[2,4,6,8] It was, in fact, the observed linear coupling between the soft quadrupolar exciton[4] and the $\langle 101\rangle$-directed TA phonon near 151 K which led to our initial Brillouin studies of $PrAlO_3$. The results of our experiments on the 151-K transition will be detailed elsewhere. Here we shall concentrate on the new transition.

The results reported here were obtained by right-angle ($\theta = \frac{1}{2}\pi$) Brillouin scattering, excited by a stabilized single-mode argon ion laser operating at 5145 Å. To avoid heating of the sample, power levels were restricted to between 10 and 20 mW. The spectra were obtained using a pressure-scanned flat Fabry-Perot interferometer. The samples were single crystals a few millimeters on a side and of a medium green color (a room-temperature absorption length for 5145-Å light of ~1 cm), grown from a $PbO \cdot PbF_2 \cdot P_2O_3$ flux. Because of previously reported[4,7,8] sensitivity to mounting strains for domain structure, etc., we employed both (a) cold-finger and (b) flowing-gas variable-temperature Dewars, with temperature stabilities of 0.01 and 0.05 K, respectively. Arrangement (b) permitted strain-free sample mounting, while (a) required bonding of the sample to the copper cold finger. Although deliberate straining did reduce the acoustic anomaly near 118 K, our usual mounting procedure gave identical results in configurations (a) and (b), indicating that any strain effects arose from internal rather than external strains. Further evidence for this came from the observed sample-to-sample variations as high as 5% in the maximum size of the acoustic anomaly near T_c. Detailed results are presented for the most strain-free samples.

Figure 1 exhibits the Stokes-Brillouin spectra for right-angle scattering [$q = (4\pi n/\lambda)\sin\frac{1}{2}\theta = 3.45 \times 10^5$ cm^{-1}; $n = 1.99$[10]] near $T_c = 118.5$ K. The two other expected acoustic modes were observed at higher frequencies, but exhibited no unusual temperature dependence. In Fig. 2 the temperature dependence of the observed elastic constant $c_{ij} = \rho V_s^2$ (where $\rho = 6.68$ g/cm^3 and $V_s = 2\pi\nu_B/q$) is

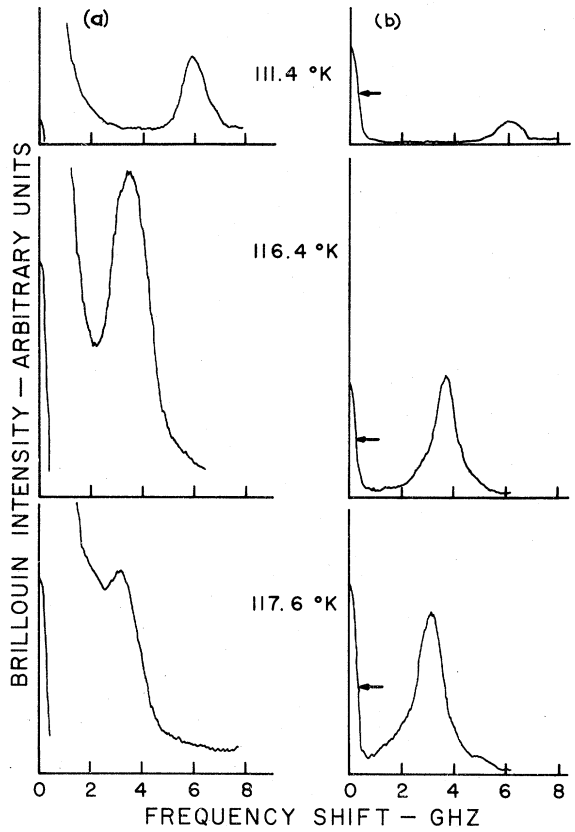

FIG. 1. Stokes-Brillouin spectra near T_c in $PrAlO_3$. (a) Without I_2 filter; elastic intensity reduced 100 ×; (b) with I_2 filter to reduce elastically scattered intensity. Arrows indicate instrumental width. Experimental geometry is $X(ZX)Y$ as discussed in the text.

shown. The following features of these results are noteworthy: (a) A nearly 99% decrease in c_{ij} occurs between 160 and 118 K. (b) Over a wide range, both above and below T_c, the anomalous temperature variation is mean-field-like ($c_{ij} = a|T - T_c|$). (c) The temperature coefficient is much larger above than below T_c ($a_> = 0.80 \times 10^{11}$ dynes/cm^2 K; $a_< = 0.10 \times 10^{11}$ dynes/cm^2 K) which differs greatly from the usual mean field ratio $(a_>/a_<)_{MF} = 2$. (d) Scattering and polarization geometries show that the new soft mode is transverse and propagates in either the $\langle 110\rangle$ or $\langle 011\rangle$ direction, polarized in the $\langle 001\rangle$ or $\langle 100\rangle$ direction. All directions are referred to cubic perovskite axes. The $\langle 010\rangle$ or b direction in the orthorhombic phase is defined as in Ref. 8, and is operationally identified in our samples by observation of the soft mode responsible for the 151-K transition, which has $\hat{q} = \langle 101\rangle$ and $\hat{e} = \langle \bar{1}01\rangle$. (e) Variation of the phonon $\hat{q}$ direction by up to ±5° (in-

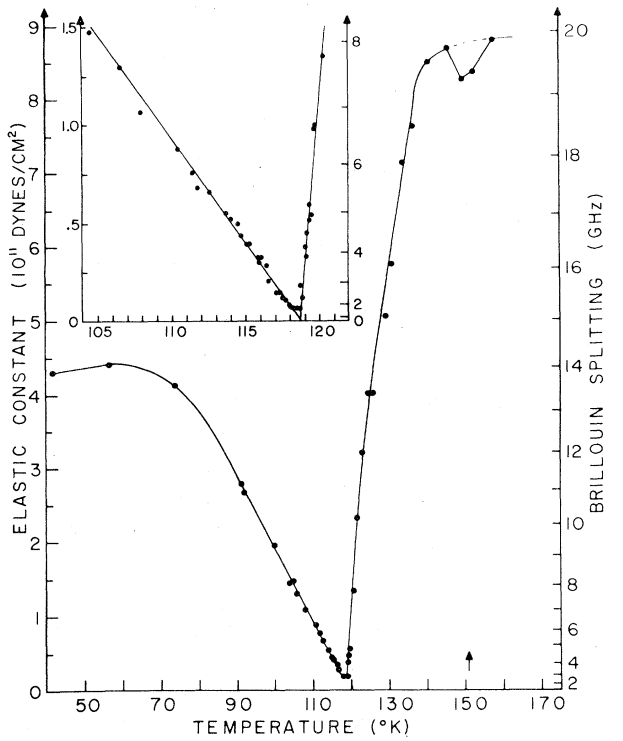

FIG. 2. Temperature dependence of soft-mode splitting ν_B (right-hand axis) and elastic constant (left-hand axis). Inset shows linear behavior of c_{ij} in $|T-T_c|$ on both sides of T_c.

ternal) with respect to the ⟨110⟩-type direction shows that contributions of nonanomalous elastic constants[12] reduce the size of the observed elastic anomaly by less than 1% when q is within ±2° of ⟨110⟩. (f) Both above and below T_c the Brillouin spectra reveal that ⟨110⟩ and ⟨$\bar{1}$10⟩ are *not* equivalent phonon propagation directions. In particular, for the "wrong" direction no softening of the TA mode is observed. This inequivalence of +45° and −45° directions relative to the b axis is incompatible with the currently accepted monoclinic[4,6] structure below 151 K. (g) An *increase* in crystal symmetry *below* T_c is implied by the observed polarization selection rules. [For the $X(\alpha\beta)Y$ scattering geometry, relative soft-mode scattering intensities of 1.0, 0.81, 0.58, and 0.33 were observed at 121 K for $\alpha\beta$ equal to ZZ, YZ, ZX, and YX, respectively. At 112 K the corresponding relative intensities were 0.03, 0.89, 1.00, and 0.05, respectively.] (h) As $T \to T_c$ and the mode softens, the scattering intensity increases. This increase is, within experimental error (±5%), in accord with the expected relation $I_B \nu_B^2 = \text{const.}$[13] (i) Very near T_c the frequency decrease saturates so that the soft mode does not actually reach zero. Among other possible reasons for this, discussed below, is the existence of a dynamic central peak arising from the soft mode as T_c is approached. However, a more detailed examination using an I_2 filter[14] to suppress elastic scattering [see Fig. 1(b)] revealed no dynamic quasielastic scattering outside the instrumental resolution (400 MHz, full width at half-maximum).

These observations (a)–(i) imply that $PrAlO_3$ undergoes a symmetry-changing (d), second-order (a) structural transition near 118 K which in some respects (b) is mean-field-like, but in others (c) not. Because of the negligible effect of this transition on quantities sensed by Raman, ESR, fluorescence, and absorption spectroscopy, together with its immense effect on the shear elastic properties, it appears that strain is the sole order parameter for this transition. Symmetry arguments applied to those transitions in which the strain is the only order parameter in the Landau sense permit only three classes of pure strain transition.[11] Two of these, which heretofore exhausted all known real examples, require that the transition be *first order*. The third permits a second-order, pure strain transition provided (a) there is a change in symmetry, and (b) all cubic and trigonal, and most hexagonal, symmetries are not involved. The only possible point of doubt regarding the admissibility of the 118-K transition to this class lies in point (i) above: the failure of the mode frequency to soften completely to zero. There could be five possible causes or contributions to this behavior: (I) The transition ultimately is first-order, albeit with at least 99% second-order character; (II) internal strain fields "round" the transition; (III) the phonon mode observed is not purely the relevant strain[12] (e.g., $\hat{q}$ could be slightly off the required axis); (IV) the emergence of a dynamic central peak may cause a saturation in the decrease of ν_B; (V) "$q\xi$" effects round the critical behavior when the inverse correlation length ξ^{-1} approaches the wave vector of the experiment.[13] For this effect to account for the observed rounding, assuming mean field behavior ($\xi^2 = \xi_0^2 |T_c/(T-T_c)|$), a value of $\xi_0 \sim 50$ Å would be required. While large, this is not unreasonable for structural transitions.[6] Measurements at much smaller $q\xi$ (e.g., ultrasonics) would resolve this aspect of the question.

Except for (I) these effects would not preclude the classification of the 118-K transition as an

Anderson-Blount transition. Based on experiments in a large number of samples, we believe that (II) is the dominant effect and is probably responsible for all the observed ν_B saturation.

Regardless of whether or not this transition strictly belongs to the Anderson-Blount class, it is of particular interest for at least two additional reasons. First, it lies entirely outside the framework of our present understanding of $PrAlO_3$ and therefore possibly of other cooperative Jahn-Teller systems. Additional symmetry complications in $PrAlO_3$ uncovered by this work pose challenges to the proper extension of these theories. Because Brillouin experiments cannot give unambiguous determination of crystal symmetry, careful neutron or x-ray studies near 118 K are needed. Second, and of perhaps wider interest, is the generality of the occurrence in perovskite-like lattices of this type of transition. Certainly it has not yet been observed in any other such material, but could easily have been missed because of the negligible coupling of the order parameter to other than acoustic probes. Although the electronic and optical phonon modes play no direct role in this transition, does it occur because of a particular set of anharmonic circumstances which themselves result from the higher temperature exciton-phonon–driven transitions in $PrAlO_3$? Unless this rather unlikely situation is indeed the case, it is quite reasonable to suppose that there are other pure-strain structural transitions in perovskite-like materials awaiting discovery.

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Note added.—Recent neutron diffraction studies (P. G. Woralton and R. A. Byerlein, to be published) of the pressure-induced phase transition[12] in TeO_2 confirm that this transition is also of the Anderson-Blount type.

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New Transport Phenomenon in a Semiconductor "Superlattice"*

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We report electronic transport properties in a GaAs-AlAs periodic structure known as a "superlattice" prepared by a molecular-beam epitaxy. Its differential conductance in the superlattice direction first gradually decreases, followed by a rapid drop to negative values, then, at high fields, exhibits an oscillatory behavior with respect to applied voltages. This observation is interpreted in terms of the formation and expansion of a high-field domain. The voltage period of the oscillation provides the energy of the first-excited band which is in good agreement with that predicted by the theory.

It has been proposed[1,2] that quantum states with desirable energies or bandwidths can be created in monocrystalline semiconductors, once a well-defined structure with extremely narrow potential barriers and wells is achieved in a controlled manner: The transport of electrons in the structure is then expected to be largely governed by such quantum states.

In this Letter, we report transport properties in a periodic structure known as a "superlattice."