Zone-Boundary Phonon Instability in Cubic $LaAlO_3$*

J. D. Axe
Brookhaven National Laboratory, Upton, New York and IBM Watson Research Center, Yorktown Heights, New York 10598

AND

G. Shirane
Brookhaven National Laboratory, Upton, New York 11973

AND

K. A. Müller
IBM Research Laboratory, Zurich, Switzerland

(Received 8 January 1969)

Inelastic-neutron-scattering measurements have been performed on the high-temperature cubic perovskite phase of $LaAlO_3$. Dispersion curves for phonons with $\mathbf{q}$ along [111] establish that near the zone corner (R point), the frequency of the lowest branch is both anomalously low and temperature-dependent. The nature of the associated scattering changes continuously from inelastic to quasi-elastic as the temperature is lowered, indicating that the soft-phonon modes become overdamped. The intensity of this quasi-elastic scattering exhibits a Curie-law divergence as the temperature is lowered further toward the transformation temperature of (535±5)°C. The displacements associated with the rhombohedral low-temperature structure result from the condensation of a particular linear combination of these soft triply degenerate Γ_{25} modes, as proposed by Cochran and Zia.

IT is well established that certain ferroelectric phase transformations result from an instability of long-wavelength ($\mathbf{q}=0$) optical-phonon modes.[1–4] The more generalized concept of displacive phase transformations, involving the condensation of phonons with finite $\mathbf{q}$, and leading to new phases with enlarged primitive unit cells, has been discussed in the literature.[1,3,5,6] Very recently, contributions of several workers have led to the confirmation that the 110°K phase transformation in $SrTiO_3$ is of this type.[7–9] The wave vector of the unstable modes is at the Brillouin-zone corner (R point) of the simple cubic perovskite structure. The displacements transform according to the triply degenerate Γ_{25} representation of the group of R, and involve rotations of the oxygen atom octahedra (we use the notation of Ref. 3 concerning symmetry properties). Subsequently, another perovskite $KMnF_3$, has been shown to undergo a similar transformation.[10]

At elevated temperatures, $LaAlO_3$ also has the cubic perovskite structure, but transforms at about 530°C into a slightly distorted rhombohedral ($R\bar{3}C$) form.[11–13] Cochran and Zia[6] have pointed out that the atomic displacements accompanying the transformation could be explained by a condensation of Γ_{25} zone-corner phonons, and the critical scattering of x rays observed by Plakhty and Cochran[12] is consistent with this interpretation. Müller *et al.*[13] have studied the atomic displacements as a function of temperature by ESR and have emphasized certain similarities between the phase transformations in $LaAlO_3$ and $SrTiO_3$. We wish to present the results of neutron scattering experiments which clearly demonstrated that the $LaAlO_3$ transformation does indeed result from an instability in the Γ_{25} phonon modes.

Measurements were carried out on a triple-axis spectrometer at the Brookhaven High Flux Beam Reactor. Inelastic scattering was performed in the "constant Q" mode with neutron energies ranging between 13 and 50 meV. The scattering was carried out in the (hll) zone of a crystal which formed a portion of a larger (~5 cm³) multicrystalline boule. Rocking curves were asymmetrical but gave an effective mosaic spread of 0.5°–1.0° FWHM (full width at half-maximum) depending upon the crystallographic orientation. The sample temperature was controlled to within ±1°C.

A comparison of the high- and low-temperature structures reveals that each Brillouin-zone corner in the extended cubic reciprocal-lattice space becomes a reciprocal-lattice point of the rhombohedral structure. We term such special positions in reciprocal space superlattice points. Figure 1 shows the observed intensity of elastically scattered neutrons about one

* Work performed under the auspices of the U. S. Atomic Energy Commission.

[1] W. Cochran, Advan. Phys. **9**, 387 (1960).
[2] A. S. Barker and M. Tinkham, Phys. Rev. **125**, 1527 (1960).
[3] R. A. Cowley, Phys. Rev. **134**, A981 (1964).
[4] G. Shirane, B. C. Frazer, V. J. Minkiewicz, J. A. Leake, and A. Linz, Phys. Rev. Letters **19**, 243 (1967).
[5] P. B. Miller and P. C. Kwok, Solid State Commun. **5**, 57 (1967).
[6] W. Cochran and A. Zia, Phys. Status Solidi **25**, 273 (1968).
[7] U. Unoki and T. Sakudo, J. Phys. Soc. Japan **23**, 546 (1967).
[8] P. A. Fleury, J. F. Scott, and J. M. Worlock, Phys. Rev. Letters **21**, 16 (1968).
[9] G. Shirane and Y. Yamada, Phys. Rev. **177**, 858 (1969); Bull. Am. Phys. Soc. **13**, 1376 (1968).
[10] V. J. Minkiewicz and G. Shirane, Bull. Am. Phys. Soc. **13**, 1376 (1968); J. Phys. Soc. Japan **26**, 674 (1968).
[11] S. Geller and V. B. Bala, Acta Cryst. **9**, 1019 (1956).
[12] V. Plakhty and W. Cochran, Phys. Status Solidi **29**, K81 (1968).
[13] K. A. Müller, W. Berlinger, and F. Waldner, Phys. Rev. Letters **21**, 814 (1968).

such superlattice point. The abrupt increase in scattering intensity beginning at $T_0=(535\pm5)°C$ is associated with the onset of Bragg scattering and establishes the transformation temperature for our sample. This is in good agreement with the value of $(527\pm10)°C$ given in Ref. 13.

This study was more concerned with the scattering about the superlattice points which persists into the cubic phase and which manifests itself in Fig. 1 as a weak high-temperature tail. Figure 2 shows an energy analysis of this superlattice scattering which, unlike true elastic Bragg scattering, is accompanied by appreciable energy transfer. Immediately above the transformation temperature the scattering is centered about $\Delta E=0$ in a broad quasi-elastic peak. As the temperature is raised, the wings of the distribution develop into well-defined peaks. Only the portion of the spectrum corresponding to neutron energy loss is shown. Since dispersion in the quasi-elastic excitations can be shown to be a relatively unimportant source of additional broadening, it is therefore clear that a major fraction of the width of the observed inelastically scattered neutron groups is to be ascribed to the finite lifetime of the excitations. Even at the highest temperatures there remains a nearly temperature-independent central component due to elastic incoherent scattering from the sample and experimental apparatus. The width of this central component (0.6-meV FWHM) is in agreement with the calculated instrumental resolution.

The essential features of these observations are consistent with the proposal of Cochran and Zia[6] involving

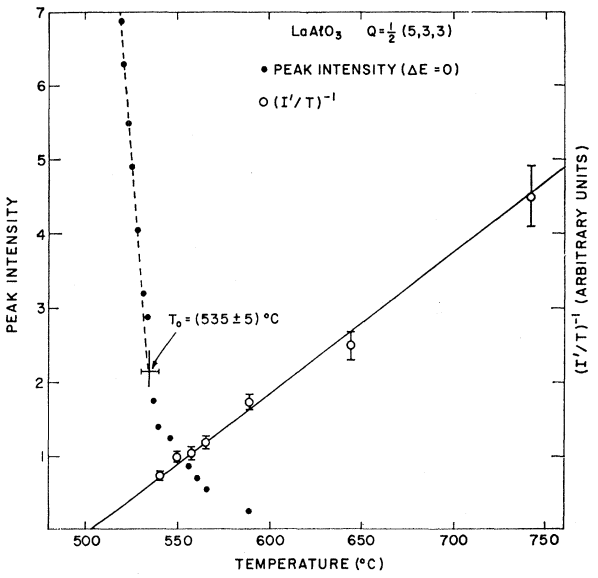

FIG. 1. The temperature dependence of the peak scattering intensity and the integrated quasi-elastic scattering intensity I' about a superlattice point in cubic $LaAlO_3$. The latter is plotted in such a way as to demonstrate an approximately Curie-law divergence.

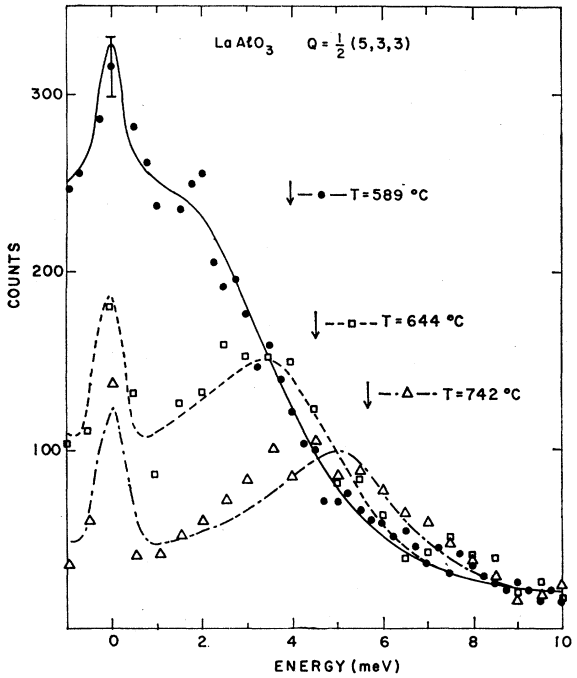

FIG. 2. Energy profile of the quasi-elastic scattering about a superlattice point in cubic $LaAlO_3$. The energy of the scattered neutrons was fixed at 25 meV. The narrow central component is due to elastic incoherent scattering from the sample and experimental apparatus. The points represent experimental measurements, and the lines, best-fitting curves of the form of Eq. (2) with the following parameters: $T=589°C$, $\hbar\omega_0=4.0$ meV, $\Gamma=5.9$ meV; $T=644°C$, $\hbar\omega_0=4.6$ meV, $\Gamma=4.2$ meV; $T=742°C$, $\hbar\omega_0=5.7$ meV, $\Gamma=3.7$ meV.

a condensation of zone-corner vibrational modes. In addition, the gradual change in the nature of the scattering from inelastic to quasi-elastic *above* the transformation temperature must be taken as an indication that the condensing modes become critically overdamped above T_0. The scattering cross section per unit cell for an anharmonic phonon mode may be written in the form[9,14]

$$\frac{d^2\sigma}{d\Omega dE}=\frac{|k'|}{|k_0|}|F_{\text{in}}(\mathbf{Q})|^2[1+n(\omega)]A(\omega), \qquad (1)$$

where $\hbar\mathbf{Q}=\hbar(\mathbf{k}_0-\mathbf{k}')$ is the momentum transfer and $\hbar\omega$ the energy transfer in the scattering event. $n(\omega)=(e^{\beta\hbar\omega}-1)^{-1}$ is the phonon occupation number, and $F_{\text{in}}(\mathbf{Q})$ is an inelastic structure factor. The phonon dynamics are described by the spectral correlation function $A(\omega)$, which for our purposes may be taken to be[15]

$$A(\omega)=\frac{1}{\pi}\frac{\omega\Gamma}{(\omega_0^2-\omega^2)^2+(\omega\Gamma)^2}, \qquad (2)$$

[14] P. C. Kwok, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1967), Vol. 20, p. 233.

[15] M. Lax, J. Phys. Chem. Solids **25**, 487 (1964).

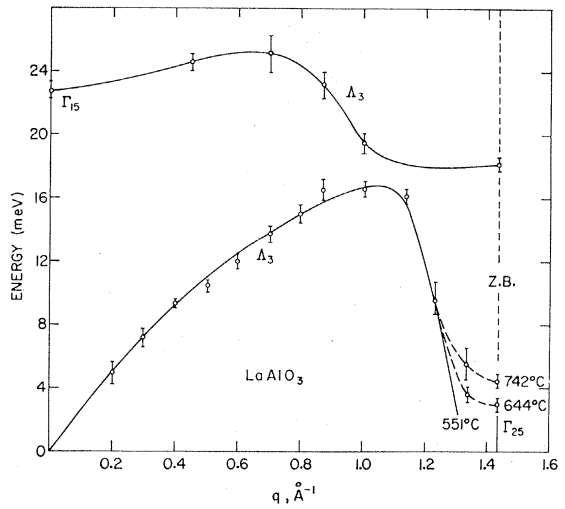

FIG. 3. Dispersion curve for the lowest transverse phonon modes with wave vectors along [111]. The major part of the data was taken at $T=551$°C with some additional data near the zone boundary to illustrate the temperature dependence of the soft modes.

where ω_0 is a renormalized temperature-dependent quasiharmonic mode frequency, and $\Gamma(\omega)$, the imaginary part of the phonon self-energy, as defined here is an even function of ω. Providing that $\Gamma(\omega)$ is well behaved and small in comparison with ω_0, the function $[1+n(\omega)]A(\omega)$ has two well-defined maxima near $\pm\omega_0$, but the peaks collapse into $\omega=0$ when $\Gamma^2=2\omega_0^2$. The character of the motion changes from damped oscillation to a pure relaxation, i.e., an $e^{-\gamma t}$ time dependence with $\gamma=\frac{1}{2}\Gamma-[(\frac{1}{2}\Gamma)^2-\omega_0^2]^{1/2}$. Although the frequency components of the fluctuations are peaked about $\omega=0$, the system is dynamically stable as long as $\gamma>0$. Thus, the condition for stability of an overdamped oscillator is the same as for an undamped one, $\omega_0^2>0$. It can be seen from Fig. 2 that the $A(\omega)$ given in Eq. (2) does provide a reasonable description of the observed scattering profiles. Here $\hbar\omega_0$ and Γ were assumed frequency-independent. Although we list the best-fitting values of these quantities, they are probably of only semiquantitative significance, since the data are uncorrected for the effect of instrumental resolution.

By analogy with other systems known to undergo displacive transformations, the energy of the condensing mode would be expected to obey the approximate relation

$$(\hbar\omega_0)^2=\alpha(T-T_c) \tag{3}$$

in a temperature range just above T_0. Although a very careful study of the neutron group energy profile would be necessary to derive the values of $\hbar\omega_0$ directly, there is an indirect method of testing Eq. (3) well suited to the present problem. Integrating Eq. (2) over energy, the integrated cross section I' of a neutron group is

$$I'\propto[T/(\hbar\omega_0)^2]|F_{\text{in}}(\mathbf{Q})|^2, \tag{4}$$

where we have used the high-temperature approximation $n(\omega)\approx 1+n(\omega)\approx kT/\hbar\omega$. A plot of experimentally determined values of $(I'/T)^{-1}$ versus temperature establishes the expected temperature dependence with $T_c=(503\pm10)$°C. By analogy with $SrTiO_3$ and $KMnF_3$, anomalous changes in the elastic behavior are to be expected in the vicinity of the transformation temperature.[16,17] It is possible that the relatively small discrepancy between T_c and T_0 occurs because the lattice becomes elastically unstable above T_c. It is also possible that sufficiently near T_0 the fluctuations are no longer adequately described by a simple $(T-T_c)^{-1}$ law.

Since the displacements associated with Γ_{25} zone-corner phonons are completely determined by symmetry considerations alone, the associated inelastic structure factor for a general superlattice point at $\frac{1}{2}(h,k,l)$ (h, k, l all odd) is found, apart from a Debye-Waller temperature factor, to be

$$|F_{\text{in}}(\tfrac{1}{2}(h,k,l))|^2\propto\Delta(h,k)+\Delta(k,l)+\Delta(h,l), \tag{5}$$

where

$$\Delta_{(i,j)}=(i+j)^2,\quad \tfrac{1}{2}(i+j)\text{ even}$$
$$=(i-j)^2,\quad \tfrac{1}{2}(i+j)\text{ odd}.$$

Intensities experimentally determined about several superlattice points appear to be in substantial agreement with these predictions and verify the symmetry of the soft mode. In particular, anomalous scattering was observed to be very weak or missing about points of the type $\frac{1}{2}(hhh)$.

Finally, we have determined phonon-dispersion curves for the two lowest transverse branches with wave vectors along the [111] direction as shown in Fig. 3. The $\mathbf{q}=0$ optic-mode frequency agrees well with the lowest observed restrahl frequency[18] and establishes the mode symmetry as Γ_{15}. Only the portion of the lower branch nearest the zone boundary shows any marked variation with temperature. In Fig. 3, we have followed the common practice of identifying the phonon energy with the peak in the scattering distribution. As we have noted, the true quasiharmonic energies are somewhat higher, although the correction is appreciable only for the soft modes near the zone boundary (see Fig. 2). In spite of the high temperatures, only in the "cross over" region near $|q|=1.1$ Å^{-1} was any difficulty encountered in resolving well-formed one-phonon neutron groups above the multiphonon background.

$LaAlO_3$ thus represents the third well-established example of a cubic perovskite which undergoes a displacive phase transformation resulting from a Γ_{25} zone-corner phonon instability. The low-temperature phase of $SrTiO_3$ is tetragonal, whereas the low-tem-

[16] R. O. Bell and G. Rupprecht, Phys. Rev. **129**, 90 (1963).
[17] K. S. Aleksandrov, L. M. Reshchikova, and B. V. Beznosikov, Fiz. Tverd. Tela **8**, 3637 (1966) [English transl.: Soviet Phys.—Solid State **8**, 2904 (1967)].
[18] Unpublished data of one of the authors (J.D.A.).

perature structure of $KMnF_3$ is reported to be orthorhombic.[19] It should be emphasized that the variety of structures possible from the same instability is a result of the degeneracy of the condensing modes. Different linear combinations of the three degenerate modes give rise to different symmetry-breaking displacements. The combination which best restabilizes the lattice is determined by anharmonic interactions as discussed in detail by Thomas and Müller.[20]

We wish to thank V. J. Minkiewicz, J. Skalyo, Jr., and H. Thomas for helpful discussions.

[19] O. Beckman and K. Knox, Phys. Rev. **121**, 376 (1967).

[20] H. Thomas and K. A. Müller, Phys. Rev. Letters **21**, 1256 (1968).

PHYSICAL REVIEW VOLUME 183, NUMBER 3 15 JULY 1969

Raman Study of Trigonal-Cubic Phase Transitions in Rare-Earth Aluminates

J. F. Scott
Bell Telephone Laboratories, Holmdel, New Jersey 07733
(Received 3 February 1969)

The Raman spectra of $LaAlO_3$, $PrAlO_3$, and $NdAlO_3$ have been observed at temperatures from 10 to 1135°K. Each of these materials evidences a nominally second-order trigonal cubic phase transition; that in $LaAlO_3$ has previously been analyzed by other workers on the basis of x-ray, EPR, and inelastic neutron scattering; however, evidence for the transitions in $PrAlO_3$ [at (1320±20)°K] and $NdAlO_3$ [at (1640±30) °K] is presented here for the first time. In each material, the phase transition is due to the collapse of the Γ_{25} mode at the R point of the high-temperature cubic Brillouin zone. Modes associated with Γ_{25} and Γ_{15} are observed in the trigonal phase in each crystal.

SINCE the early work of Wood,[1] $LaAlO_3$ has been known to undergo a transition to a cubic phase at ~800°K. A crystallographic analysis of this $D_{3d} \rightarrow O_h$ transition was made by Geller and Bala[2] in a paper which also characterized $NdAlO_3$ and $PrAlO_3$ as D_{3d} and suggested the possibility of equivalent phase transitions in the latter materials at temperatures above 1223°K (the limit of their investigation). More recently, theoretical analysis of the $LaAlO_3$ transition has been presented,[3] along with EPR data,[4] which shows that the transition involves a unit-cell doubling brought on by the collapse of the Γ_{25}-phonon branch at the R point of the high-temperature Brillouin zone. The order parameter for the phase transition is inferred[4] to be the angle of rotation of the oxygen octahedra. This transitional-cubic transition in $SrTiO_3$, which was first deciphered on the basis of Raman studies.[5] The behavior of the soft Γ_{25} mode in the cubic phase of $LaAlO_3$ has been very recently reported[6]; it is the intent of the present paper to characterize the D_{3d}-phase modes and to examine the transitions in $NdAlO_3$ and $PrAlO_3$.

[1] E. A. Wood, private communication cited in Ref. 2; see also Am. Mineralogist **36**, 768 (1951).
[2] S. Geller and V. B. Bala, Acta Cryst. **9**, 1019 (1956).
[3] W. Cochran and A. Zia, Phys. Status Solidi **25**, 273 (1968).
[4] K. A. Müller, W. Berlinger, and F. Waldner, Phys. Rev. Letters **21**, 814 (1968).
[5] P. A. Fleury, J. F. Scott, and J. M. Worlock, Phys. Rev. Letters **21**, 16 (1968); in *Light Scattering Spectra of Solids*, edited by G. B. Wright (Springer-Verlag, New York, 1969), pp. 689–696.
[6] J. D. Axe, G. Shirane, and K. A. Müller, Bull. Am. Phys. Soc. **14**, 61 (1969).

EXPERIMENTAL

The data were obtained with an argon-ion laser emitting approximately 1 W. The $NdAlO_3$ spectrum was recorded with 4880 Å excitation; $LaAlO_3$ and $PrAlO_3$ were studied at 5145 Å. In each case the emission wavelength was dictated by fluorescence problems. Detection was via a Spex 1400 double monochromator and counting electronics, with a cooled EMI6256 phototube and a Keithley 610B electrometer. The crystals were mounted in a conventional helium Dewar for low-temperature work. At elevated temperatures, a tubular alumina furnace (Norton Company) with quartz viewing windows was employed; the collection optics consisted of a 200-mm f/2.8 camera lens mounted outside the furnace. The $LaAlO_3$ sample was supplied by Union Carbide. It was a cube of ~0.5-cm side, cut from a melt-pulled boule. It was detwinned via the method of Fay and Brandle.[7] The $PrAlO_3$ and $NdAlO_3$ samples were grown from flux by Van Uitert. Single crystals of excellent optical quality and 2-mm dimension were mounted in a platinum holder. Typical data are shown in Fig. 1.

THEORY

While Geller and Bala suggested D_{3d}^5 (or $R\bar{3}m$) as the most probable space group for these rare-earth aluminates, more recent work by Denighetti *et al.*[8] sug-

[7] H. Fay and C. D. Brandle, J. Appl. Phys. **38**, 3405 (1967).
[8] B. Denighetti, J. E. Drumheller, F. Laves, K. A. Müller, and F. Waldner, Acta Cryst. **18**, 557 (1960).