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.

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

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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 $PrAlO_3$.

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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-

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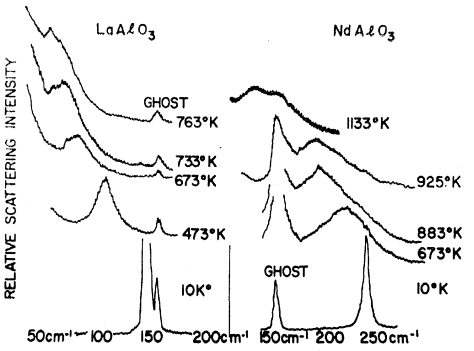

FIG. 1. Typical spectra of $LaAlO_3$ and $NdAlO_3$. Scattering intensity (arbitrary units) is plotted versus frequency shift (cm^{-1}) from the laser line for several temperatures. Spectral slit widths were 3 cm^{-1} at low temperatures and 10 cm^{-1} at high temperatures.

gests a greater likelihood of D_{3d}^6 (or $R\bar{3}c$). The D_{3d}^5 structure would have Al ions at D_{3d} $(\bar{3}m)$ sites, La ions at C_{3v} $(3m)$ sites, and oxygen ions at C_s (m) sites, resulting in a division of the 30 vibrational degrees of freedom per unit cell into modes of the following symmetries at the zone center:

$$\Gamma(D_{3d}^5)=A_{1u}+A_{2g}+3A_{1g}+5A_{2u}+4E_g+6E_u.$$

The D_{3d}^6 structure would have Al ions at C_{3i} $(\bar{3})$ sites, La ions at D_3 (32) sites, and oxygen ions at C_2 (2) sites, resulting in a very different symmetry division of normal modes:

$$\Gamma(D_{3d}^6)=2A_{1u}+3A_{2g}+A_{1g}+4A_{2u}+4E_g+6E_u.$$

A full correlation of D_{3d}^6 and D_{3d}^5 zone-center phonon modes with those at the R point of the O_h^1 structure is given in Table I. It is to be noted that the present data are insufficient to distinguish between the two trigonal space groups. However, the D_{3d}^5 space group is *not* consistent with a Γ_{25}-phonon collapse at the R point, which requires that the Al ions have C_{3i} symmetry and not D_{3d} in the trigonal phase. Since Axe *et al.*[6] have shown that Γ_{25} does soften at R, it follows that D_{3d}^6 is

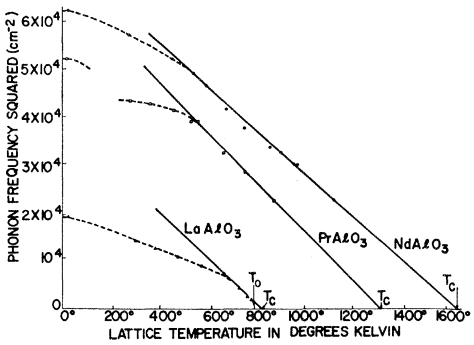

FIG. 2. Plot of ω^2 versus temperature for the soft A_{1g} modes in $LaAlO_3$, $PrAlO_3$, and $NdAlO_3$. The straight lines are the suggested Curie-law dependences. Their intersections with the base line are the implied transition temperatures T_c, which are $\geq$ the actual phase-transition temperatures T_0.

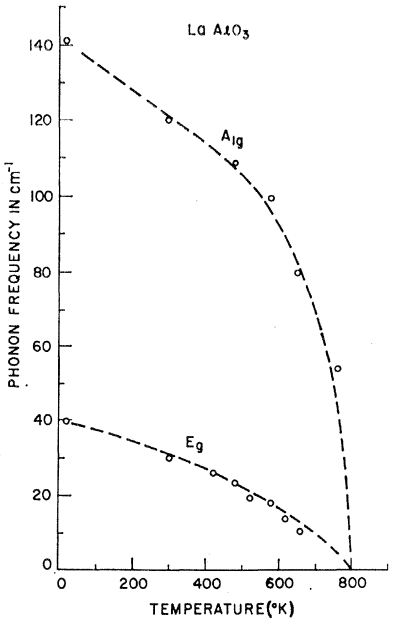

FIG. 3. Phonon frequencies of the A_{1g} and E_g soft modes in $LaAlO_3$. The smooth curves are only suggested and are constrained to become degenerate at zero frequency at ~800°K.

the correct space group, and we have included the D_{3d}^5 analysis in Table I for completeness only.

DISCUSSION

Figure 2 displays a plot of phonon frequency squared versus temperature. The phonon branch plotted in each case is that of the A_{1g} mode associated with Γ_{25}. The E_g component of Γ_{25} was also observed, and is shown in Fig. 3 for $LaAlO_3$. (A typical set of experimental curves is shown in Fig. 4.) The other Raman features were observed at ~500 cm^{-1}, and we associate

TABLE I. Mode correlation for phonons at the point R in the O_h^1 Brillouin zone and at Γ in the D_{3d}^5 and D_{3d}^6 Brillouin zones.

O_h^1 mode symmetry	D_{3d}^5 mode symmetry	D_{3d}^6 mode symmetry	Frequency at 300°K (cm^{-1}) $LaAlO_3$	$PrAlO_3$	$NdAlO_3$
$F_{2u}(R)\Gamma_{25}$	$E_g(\Gamma)$	$E_g(\Gamma)$	33	44	50
	$A_{1g}(\Gamma)$	$A_{1g}(\Gamma)$	122	214	241
$F_{1u}(R)\Gamma_{15}$	$E_g(\Gamma)$	$E_g(\Gamma)$			
	$A_{ig}(\Gamma)$	$A_{2g}(\Gamma)$			
$E_u(R)\Gamma_{12}'$	$E_g(\Gamma)$	$E_g(\Gamma)$	470? (weak)		
$F_{1u}(R)\Gamma_{15}$	$E_g(\Gamma)$	$E_g(\Gamma)$	487	504	509
	$A_{1g}(\Gamma)$	$A_{2g}(\Gamma)$			
$F_{2g}(R)\Gamma_{25}'$	$E_u(\Gamma)$	$E_u(\Gamma)$			
	$A_{2u}(\Gamma)$	$A_{1u}(\Gamma)$			
$A_{2u}(R)\Gamma_2'$	$A_{2g}(\Gamma)$	$A_{2g}(\Gamma)$			
$3F_{1u}(\Gamma)$	$3E_u(\Gamma)$	$3E_u(\Gamma)$			
	$3A_{2u}(\Gamma)$	$3A_{2u}(\Gamma)$			
$F_{2u}(\Gamma)$	$E_u(\Gamma)$	$E_u(\Gamma)$			
	$A_{1u}(\Gamma)$	$A_{1u}(\Gamma)$			

them with Γ_{15} on the basis of their frequency and a comparison with $SrTiO_3$.[5]

The temperature dependence of the A_{1g} branch of each of the materials obeys a Curie law $[\omega^2\alpha(T_c-T)]$ above 600°K, but flattens out at low temperatures. The E_g branches also exhibit a similar dependence. T_c extrapolated from our data is (840±20)°K for $LaAlO_3$, (1320±20)°K for $PrAlO_3$, and (1640±30)°K for $NdAlO_3$. These T_c represent upper limits for the actual phase-transition temperatures T_0. The two will be coincident if the transition is exactly of second order; deviation from second order will be evidenced by the amount by which T_c *exceeds* T_0. In $LaAlO_3$ our results differ slightly from the EPR-determined T_0. These observations may, however, be due to the uncertain reliability of a Curie-law fit to the $LaAlO_3$ data or to uncertainties in the sample temperature, since the results of Ref. 4 assign the transition as unquestionably of second order.

The anomalous temperature dependence of the phonon frequency in $PrAlO_3$ near room temperature is due to the presence of two lower-temperature phase transitions currently under study by Cohen and Riseberg.[9] Note that, in relation to the inferred transition temperatures T_c in Fig. 2, the melting points for all of these materials is ~2080°K.[10]

An attempt at an analysis of the phonons in $CeAlO_3$ is still under way. On the basis of its known structure[11] and the ionic radius of Ce, it is expected to have a second-order phase transition at ~1100°K. We have found thus far only the spectrum of what we assume is CeO_2 (CaF_2 structure), whose F_{2g} mode is at 466 cm^{-1} at 295°K and 456 cm^{-1} at 773°K.

Note added in proof. After the submission of this paper, new high-temperature x-ray data on $PrAlO_3$ were obtained by Dr. S. Geller and communicated to the author. Dr. Geller finds $PrAlO_3$ is still trigonal at 1400°K (80°K above the transition temperature inferred in Fig. 2) with a rhomb angle 5 min of arc larger than the 60° occurring in the O_h^1 phase. The data presented in this paper were obtained with a calibrated thermocouple mounted on the sample; the system was checked with the quartz transition at 846°K and found to be accurate within 5°K. Consequently the disagreement between our inferred transition temperature and Geller's higher estimate suggest that the ω^2 linear in (T_c-T) molecular field extrapolation made in Fig. 2 is not quite valid, despite good agreement with lower-temperature data. The quoted uncertainties of ±20 and ±30°K for T_c in this paper do not, of course, assess systematic errors involved in the extrapolation. The values of T_c given in the text are only the best estimates obtainable from the existing Raman data. Geller's new data suggest my estimates are at least 10% low.

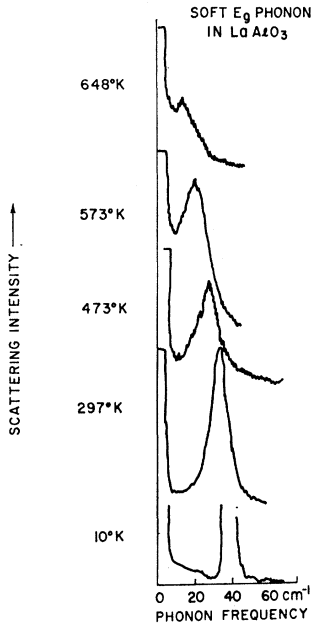

FIG. 4. Soft E_g mode in $LaAlO_3$.

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