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High-Temperature Raman Study of Samarium Aluminate

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Raman spectra of an oriented single crystal of $SmAlO_3$ have been obtained at temperatures from 10 to 970°K. The temperature dependences of phonon frequencies and scattering cross sections are correlated with structural changes occurring at elevated temperatures. Three phonon modes are observed to soften (decrease) in frequency as the temperature is increased. The hypothesis is put forth that these soft modes are not dynamically associated with the known $V_h^{16} \rightarrow D_{3d}$ phase transition at $\sim$1100°K, but rather with a previously unsuspected $D_{3d}^6 \rightarrow O_h^1$ phase transition near the melting point. The soft-mode frequencies are discussed in terms of an anharmonic potential, and it is shown that the sign of a quartic term is opposite that of $LaAlO_3$, $PrAlO_3$, and $NdAlO_3$.

INTRODUCTION

The lattice structure of rare-earth aluminates is known primarily from the x-ray studies of Geller and Bala,[1] who inferred trigonal D_{3d} symmetry for the aluminates of the lighter rare earths La, Pr, and Nd, and orthorhombic V_h symmetry for Y, Gd, Eu, and $SmAlO_3$.

They also presented evidence for a $D_{3d} \rightarrow O_h$ second-order phase transition in $LaAlO_3$, and a $V_h \rightarrow D_{3d}$ first-order phase transition in $SmAlO_3$. Since the time of their work several advances have been made in the theoretical and experimental study of pseudoperovskites.

First it was shown[2] that the most probable space group for the trigonal aluminates was D_{3d}^6, rather than the D_{3d}^5 inferred by Geller and Bala. Then both theoretical calculations[3] and EPR studies[4] showed that the $LaAlO_3$ transition was triggered by the collapse of the Γ_{25} optical-phonon branch at the R point (corner) of the simple cubic Brillouin zone. The temperature dependence of the optical phonons involved were determined by inelastic neutron scattering in the high-temperature phase[5] and by Raman spectroscopy in the low-temperature phase.[6] Dynamically equivalent phase transitions were shown to exist in $SrTiO_3$,[4,7] $PrAlO_3$, and $NdAlO_3$.[6] And an anharmonic model was used to describe the lattice dynamics of the materials; an expansion of the lattice potential to terms up to quartic sufficed to describe most of the experimental observations.[8] Subsequently, two new low-temperature phase transitions were discovered in $PrAlO_3$[9]: a second-order $C_i \rightarrow V_h$ transition and a first-order $V_h \rightarrow D_{3d}$ transition. In addition, $CeAlO_3$ was shown[10] to share the D_{3d}^6 structure of the aluminates of cerium's neighbors in the Periodic Table.

The purpose of the present work is to investigate the lattice dynamics of $SmAlO_3$ and to assess the experimental data relating to lattice instabilities in that material. In particular, we present evidence that $SmAlO_3$ becomes very nearly the ideal cubic perovskite lattice at temperatures slightly below its melting point. The quartic anharmonic potential of Thomas and Muller is employed to analyze the "soft" phonon data, and comparisons are made with $PrAlO_3$, $NdAlO_3$, and $LaAlO_3$.

EXPERIMENTAL

The samples were grown by a method previously described for the growth of rare-earth orthoferrites[11]; they were yellow single crystals approximately 1×2×5 mm, with good optical quality, having a high degree of transparency, and no flaws visible to the eye. They exhibited growth faces along the $[1\bar{1}0]$, $[110]$, and $[001]$ pseudocube axes. A $[100]$ face was cut on each sample, and Raman spectra were obtained with the incident laser beam propagating along $[001]$ and the scattered light along $[100]$, which we shall denote, respectively, as Z and X. An argon-ion laser emitting 100 mW at 5145 Å was employed. (The samples were found to be highly absorbing at 4880 Å.) Detection was by means of a Spex double monochromator, a

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cooled EMI-6256 photomultiplier, and a Keithley 610B electrometer. At elevated temperatures the samples were mounted in an alumina furnace. Temperatures were monitored with a calibrated thermocouple mounted within $\frac{1}{8}$ in. of the sample (but not in thermal contact with the crystal). Temperature measurements were reproducible to about 5°K and the absolute error was estimated to be about 5°K also, by examination of the quartz transition at 573°C.

For the V_h point group totally symmetric A_g vibrations exhibit trace (xx, yy, and zz) scattering and B_{1g}, B_{2g}, and B_{3g} modes exhibit, respectively, xy, xz, and yz nonzero Raman tensor elements. Experimental geometries employed were, in the usual notation, $z(yy)x$, $z(xy)x$, $z(xz)x$, and $z(yz)x$. Hence phonon propagation was along $[\bar{1}01]$ in each case.

Representative 297°K data for each polarization are shown in Fig. 1. Of the $7A_g+5B_{1g}+7B_{2g}+5B_{3g}$ Raman-active modes predicted theoretically for the room-temperature lattice with four formula groups per primitive cell, less than half have been observed.

The symmetry assignments in Fig. 1 are ambiguous. While we were able to locate the principal axes of our samples with x-ray techniques, the exceedingly small deviation from cubic structure did not allow us to unambiguously assign a, b, c axes ($a\approx b\approx c'\approx c\sqrt{2}$ within 0.005 Å). Hence we have resorted to the notation $B_g(xy)$, $B_g(xz)$, and $B_g(yz)$ to designate the three even-parity, nontotally symmetric species which would be B_{1g}, B_{2g}, and B_{3g} if x, y, and z laboratory-frame coordinates correspond to a, b, and c crystallographic axes.

DISCUSSION

$SmAlO_3$ undergoes a first-order displacive phase transition near 800°C from a V_h^{16} structure with four formula groups per primitive cell to a D_{3d}^6 space-group lattice with two formula groups per primitive cell.[1] The distortions involved are quite small. It is known[6] that only two strong Raman lines are present in D_{3d}^6 aluminates; one of these two lines is doubly degenerate. The degeneracy is removed in the V_h orthorhombic phase and thus three strong Raman lines are expected to persist to lower temperatures. In addition, many phonons which were at the edge of the D_{3d}- phase Brillouin zone become Raman-active in the V_h phase by virtue of the additional reciprocal-lattice points created by the unit-cell doubling phase transition. If the $D_{3d}\rightarrow V_h$ distortion is small, the Raman intensities of these new zone center phonons should also be small, since they are zero in the limiting case of no distortion.

The above description is entirely compatible with the data. Above 300°K only three strong lines persist in the Raman spectrum—an intense A_g mode at $\sim$76 cm^{-1} and two nontotally symmetric $B_g(xy)$ and $B_g(yz)$ modes at $\sim$143 and 170 cm^{-1}. At 4°K many very weak modes are present, most of which disappear by 300°K, all of which are gone by 700°K. Hence we conclude

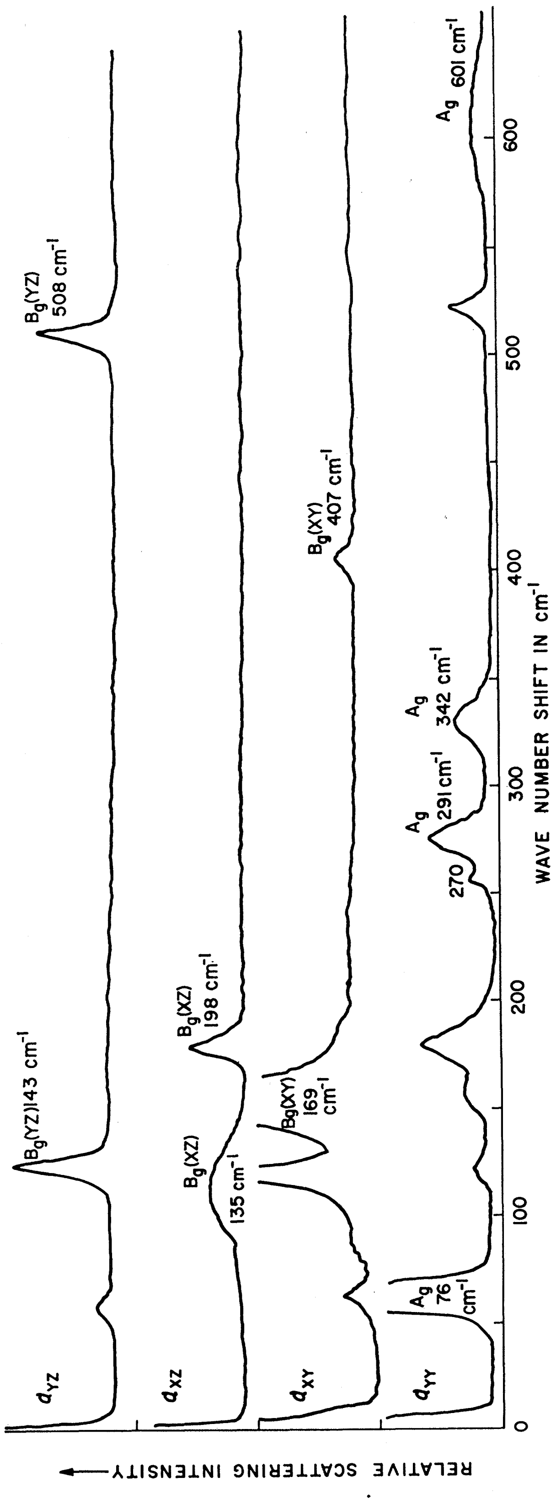

FIG. 1. Raman spectra of $SmAlO_3$ at 297°K.

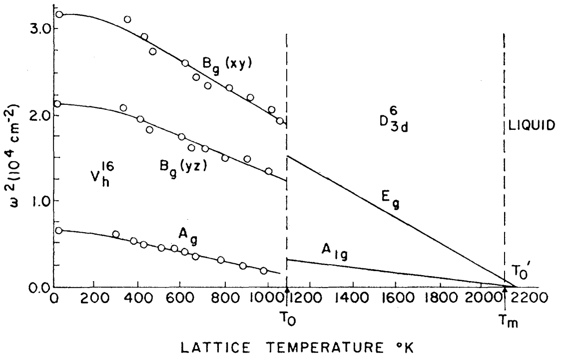

FIG. 2. Temperature dependence of soft optical phonons in the V_h^{16} phase of $SmAlO_3$, with speculated extrapolation to the D_{3d}^6 phase.

that in the D_{3d}^6 phase the $B_g(yz)$ and $B_g(xy)$ modes coalesce into an E_g vibration and the symmetry designation of the totally symmetric mode changes from A_g to A_{1g}.

Figure 2 shows that these three V_h phase modes "soften" (lower) in frequency as the temperature is raised, but have no obvious connection with the $V_h \rightarrow D_{3d}$ phase transition temperature. The behavior of the E_g and A_{1g} soft modes in D_{3d}^6 structure aluminates has been the subject of analysis in Refs. 3–8. The primary point of the present paper is illustrated schematically in Fig. 2: that the soft modes in the V_h phase of $SmAlO_3$ are not associated with the $V_h \rightarrow D_{3d}$ transition at ~800°C, but rather with a heretofore unsuspected transition to the ideal O_h^1 structure near (or above) the melting point.

In Fig. 2 an extrapolation of the phonon frequencies has been made to higher temperatures. The phonon frequencies are expected to be independent of temperature near absolute zero, to vary as $(T_0-T)^{1/2}$ over a substantial range of higher temperatures where the molecular-field approximation is valid, and to exhibit small discontinuities at the first-order transition near 800°C. The extrapolation indicates a likely $D_{3d}^6 \rightarrow O_h^1$ second-order phase transition near the melting point T_m.

While the extrapolation shown in Fig. 2 does not seem sufficiently reliable to provide information about the existence of a real O_h^1 phase below the melting point, this line of analysis does permit several useful comparisons. First, we observe the $D_{3d}^6 \rightarrow O_h^1$ transition temperatures inferred for $LaAlO_3$, $PrAlO_3$, $NdAlO_3$, and $SmAlO_3$ (800°K, 1320°K, 1640°K, ~2100°K) vary inversely and monotonically with the radius of the rare-earth ion. Since only an inner electron shell is being filled, this transition temperature is apparently a very sensitive parameter.

Secondly, the assignment in Fig. 2 of the $B_g(xy)$ and $B_g(yz)$ soft modes as the progeny of the E_g D_{3d}^6 soft mode permits utilization of the anharmonic potential of Thomas and Muller[8] for analysis:

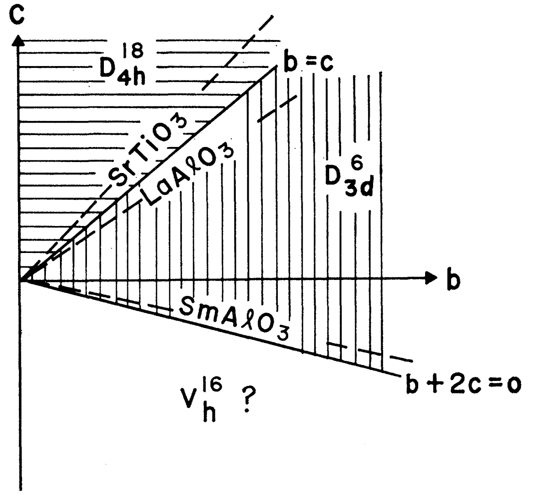

FIG. 3. Anharmonic potential coefficients in several pseudoperovskites (after Ref. 8).

$$V=V_0(T)+\tfrac{1}{2}a(T)(\Phi_x^2+\Phi_y^2+\Phi_z^2)+\tfrac{1}{4}b(T)(\Phi_x^4+\Phi_y^4+\Phi_z^4)+\tfrac{1}{2}c(T)(\Phi_x^2\Phi_y^2+\Phi_y^2\Phi_z^2+\Phi_z^2\Phi_x^2).$$

The coefficients a, b, and c can be shown[6] to be slowly varying functions of temperature in the rare-earth aluminates. Thomas and Muller have found[8] that this potential leads to no stable structure if $b<0$, to the D_{4h} $SrTiO_3$ structure if $0<b<c$, and to the D_{3d} $LaAlO_3$ structure if $b>c$ and $b>-2c$. For the trigonal case one finds[12] that $\omega_E^2/\omega_A^2=(b-c)/(b+2c)$. Hence if the frequency ω_E of the E_g mode is greater than that ω_A of the A_{1g} mode, c is negative. In the previously examined cases of $LaAlO_3$, $PrAlO_3$, and $NdAlO_3$, c was positive and only a little less than b.[6] According to the analysis of Thomas and Muller this implies that those aluminates are very nearly unstable against the D_{4h} distortion.

In the present case of $SmAlO_3$ if we approximate the E_g frequency ω_E in the D_{3d} phase as the average of $B_g(xy)$ and $B_g(yz)$ frequencies in the V_h phase, we find that

$$\omega_E^2/\omega_A^2=(b-c)/(b+2c)\approx 4,$$

or $c\cong -\tfrac{1}{3}b$. Compared to $LaAlO_3$, $PrAlO_3$, and $NdAlO_3$ values, this is at the opposite end of the allowed range for c given by Thomas and Muller. It is far from the tetragonal structure, and near the extreme limit of stable structure given[8] by $c=-\tfrac{1}{2}b$.

This is, of course, compatible with the actual observations of a first-order transition from D_{3d}^6 to V_h^{16}. Thomas and Muller's analysis was implicitly restricted to second-order phase transitions from the cubic O_h^1

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[12] Dr. N. R. Werthamer has pointed out that Eq. (19) in Ref. 8 should read $\omega_E=[\tfrac{2}{3}(b-c)]^{1/2}\Phi$ and not $\omega_E=[\tfrac{2}{3}(b-2c)]^{1/2}\Phi$.

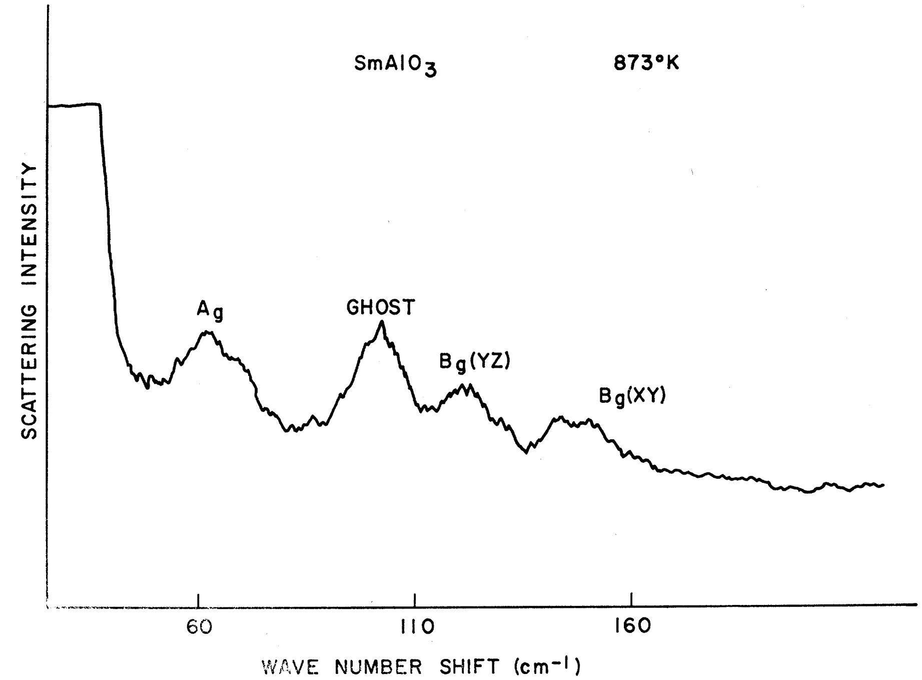

FIG. 4. Raman spectrum of $SmAlO_3$ at 873°K.

structure. Hence their predictions of no stable structure for $c<-\frac{1}{2}b$ may be interpreted as diagnosing $D_{3d}{}^6$ structure with $c\approx-\frac{1}{2}b$ as unstable against an unspecified first-order distortion, which empirically is found to be $D_{3d}{}^6 \rightarrow V_h{}^{16}$. This is diagrammed in Fig. 3.

SUMMARY

In conclusion, we find evidence for interpreting three soft modes in $SmAlO_3$ as progeny of Γ_{25} of the ideal cubic perovskite lattice and indications that a transition from $D_{3d}{}^6$ to that $O_h{}^1$ structure may take place near the melting point. No soft modes associated with the first-order $V_h \rightarrow D_{3d}$ transition have been observed. A simple empirical connection between $D_{3d} \rightarrow O_h$ transition temperatures in rare-earth aluminates has been made. And a quartic potential coefficient has been inferred to be of opposite sign to that in the isomorphic lattices $LaAlO_3$, $PrAlO_3$, and $NdAlO_3$.

It is obviously desirable to extend the Raman measurements of $SmAlO_3$ into the temperature region in which it has $D_{3d}{}^6$ structure, in order to directly confirm the predictions made in this paper. An attempt was made to extend the present experiment to 1200°K but was wholly unsuccessful, due to blackbody radiation from the sample. At 1000°K the emission was intense enough to obscure all Raman spectra excited by the 5145 Å laser; chopping the beam and synchronously detecting the scattered light failed to overcome phototube noise saturation. (See Fig. 4 for typical high-temperature data.) The suggested remedy of this emission problem in future high-temperature work is the use of uv excitation, such as the CdII laser.

There is some additional motivation for further light scattering studies in $SmAlO_3$ at very low temperatures, since de Combarieu *et al.* have shown[13] that it is antiferromagnetic below 1.3°K. In the present study spectral measurements were made down to ~10°K and exhibit no anomalies at such temperatures. The λ-type magnetic ordering inferred at 1.3°K apparently has very little effect upon the lattice structure and phonon frequencies. Raman scattering from two-magnon excitations in the paramagnetic phase[14] was not observed and indeed would be expected to be several orders of magnitude weaker than the phonon scattering.

ACKNOWLEDGMENT

We thank L. E. Cheesman for technical assistance.

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