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Raman scattering from solid argon at high pressure

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Second-order Raman scattering from solid argon at low temperature exhibits sharp features corresponding to van Hove singularities arising from critical points in the joint phonon density of states. The singularities observed in a crystal grown at 10 kbar compare favorably with those calculated at a lower density after the frequencies are scaled. Comparison of the calculated relative intensities of these features with those observed shows that the coupling between pairs of longitudinal phonons has been underestimated while the coupling between phonons of different branches has been exaggerated. The variation of spectral intensity and shape measured from low temperature (12 K) to near melting (256 K) can be attributed to the changing occupation numbers of the phonon pairs and smoothing of the joint density of states as the temperature rises. In addition, an average mode Grüneisen parameter of value 2.67 was measured relative to a crystal grown at 5 kbar.

INTRODUCTION

Rare-gas solids at low temperature have traditionally provided a proving ground for development of lattice dynamic theories. Highly successful theories were developed first for the heavier elements, where zero-point motion is minimal, and later for the quantum solids, where anharmonicities and short-range correlations must be considered.[1] Recently, the lattice dynamics of argon near melting was calculated using an existing formalism;[2] excellent agreement was found with the dispersion curves measured by neutron scattering[3] at 81 K. Current lattice dynamic approaches may be further tested by examining the volume dependence of argon dynamics. It is now possible for lattice dynamics to be studied experimentally at megabar pressures with the advent of the diamond anvil cell. Light scattering experiments will most likely provide the first measurements[4] of lattice dynamics in rare-gas solids at extreme pressures owing to the difficulties associated with measurements of neutron scattering in a diamond-avil cell. We report here a study of second-order Raman scattering from argon at pressures up to 10 kbar as a step in the direction of ultrahigh pressures.

Second-order Raman scattering provides an alternate means for measuring the phonon density of states and the critical points of a crystal. The sum process of second-order scattering results in photons lowered in energy by the amount taken away by the pair of created phonons. These phonons are oppositely directed with nearly canceling momenta since the photon carries momentum negligible compared to that of a phonon. The intensity of scattering at a particular Raman frequency will be proportional to the number of pairs of phonons with this total energy and capable of satisfying the conservation of momentum condition. Sharp features arise in the Raman spectrum corresponding to singularities in the joint density of states. There are more features in the joint density of states than in the simple density of states owing to the larger number of possibilities for satisfying the zero-slope condition when considering sums of dispersion curves. The intensity of scattering also depends on the polarizability associated with the different phonons involved. Second-order Raman scattering thus provides a polarizability-weighted measure of the joint density of states. All singularities are measured directly without recourse to fitted models, provided that the individual phonons have narrow linewidth and are resolvable by the Raman spectrometer.

Second-order spectra from crystals of argon grown at 5 and 10 kbar have been measured over a wide range of temperature, from 12 K to melting. Sharp features in the low-temperature spectra have previously been exhibited in argon[5] and xenon,[6] but were somewhat obscured by counting noise and stray light at low-scattering frequencies. The current study was motivated partly by the recent success in observing the density and temperature dependence of the energy and lifetime of the low cross section Raman-active phonon in hcp helium at high pressure.[7] With the improvements in signal-to-noise obtained in that study, it was anticipated that a reexamination of Raman scattering from argon might provide additional information about the density and temperature dependence of its lattice dynamics. Study of the detailed evolution of the Raman spectrum with temperature was also intended to provide groundwork for the study of argon alloys at high pressure.

Raman spectra were obtained with laser excitation of 250 mW (500 mW above 80 K) at 488 nm, a conventional Raman spectrometer, and photon-counting electronics using a Channeltron photomultiplier with low dark count (8 counts/min). Argon crystals were grown in a high-pressure optical cell by slowly increasing pressure to cross the melting curve at the desired temperature of growth, with a temperature gradient across the cell so that the crystal grew towards the fill capillary. The subsequent tubing blockage isolated the crystal from the rest of the high-pressure system. Crystal density values were based on careful measurement of the melting temperature and reported values of molar volume (estimated uncertainty of 0.02 cm^3/mol) on the melting curve.[8] Crystals were grown at 254.3 K (10 kbar) and 180.5 K (5 kbar) having molar volumes of 20.61 and 22.05 cm^3/mol, respectively.

RELATIVE INTENSITIES

The spectra obtained at 12 K from both crystals show the same distinct features, although the middle part of the low-density spectrum is somewhat obscured (Fig. 1.) The additional peak in the high-density spectrum arises from a laser plasma line in the incident light which was not entirely rejected by a narrow pass filter. Plasma lines at 37, 103, and 220 cm^{-1} were observed in the high-density spectra. A laser filter monochromator was acquired and successfully used to prevent plasma lines in the low-density spectra.

The relative strengths of the various features are surprisingly similar in both crystals. Crystal orientation was not determined but would appear to be the same for each crystal, although it is possible that the samples were polycrystalline. The good optical quality of the samples within the scattering volume (6 mm × 80 μm) and the slow crystal growth followed by annealing would argue against the samples being polycrystalline however. The second-order spectrum of single-crystal argon should exhibit an orientational dependence, since the Raman cross section is a fourth-rank tensor.[9] The induced-dipolar model used by Werthamer *et al.* limits the tensor to two independent elements, S_{11} and S_{44}, for a fcc crystal. The observed Raman spectrum is thus a weighted average of these components, where the weighting is dependent on the orientation. The weighting for a polycrystalline sample, $\frac{3}{5}(\frac{1}{2}S_{11}+S_{44})$, provides the best agreement with the observed relative strengths of the spectral features even though the sample is probably not polycrystalline (see Fig. 2).

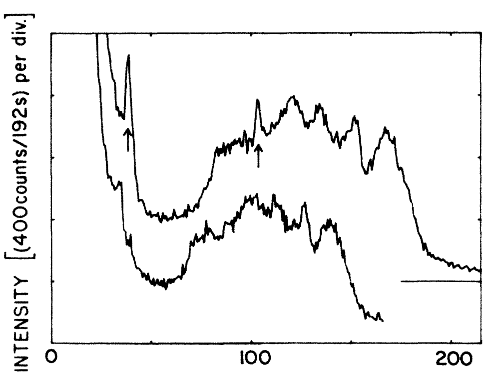

FIG. 1. Second-order Raman spectra of solid argon. The lower and upper spectra were obtained from crystals grown at 5 and 10 kbar and cooled to 12 and 25 K, respectively. The spectral features correspond to singularities in the joint density of phonon states; the arrows indicate laser plasma lines. Spectra are offset vertically for clarity.

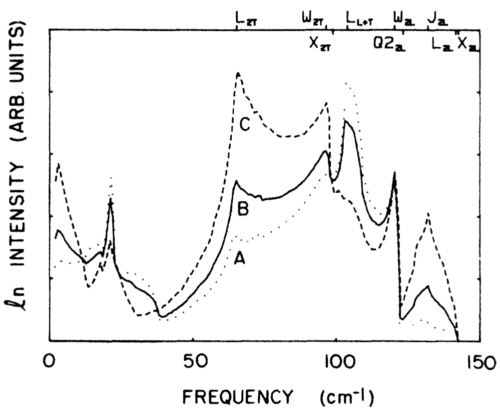

FIG. 2. Computed Raman spectra of solid argon. Spectra A and C, extracted from Ref. 6, represent elements S_{44} and S_{11}, respectively, of the Raman tensor computed with a point-dipole model of polarizability. Spectrum B, the polycrystalline-weighted average of these elements, exhibits all of the features that arise from two-phonon sum (above 50 cm^{-1}) and difference (below 50 cm^{-1}) processes. The symmetry points on the Brillouin-zone edge [L: (0.5,0.5,0.5), W: (1,0.5,0), X: (1,0,0), Q_2: (0.56,0.56,0), and J: (0.1,0.1,0.8)] and the type of phonons (L longitudinal, T transverse) responsible for each singularity in the spectrum are indicated.

In Fig. 3 the high-density spectrum is compared to one scaled from a calculation for a density of 22.1 cm^3/mol (which also includes difference processes at low frequencies).[10] The shapes of the observed features compare favorably with the calculated singularities. The agreement with the peak labeled W_{2L} in Fig. 2, two longitudinal phonons at the W critical point, is particularly eye catching. In fact this feature has the same strength for any orientation and has been used to set the intensity

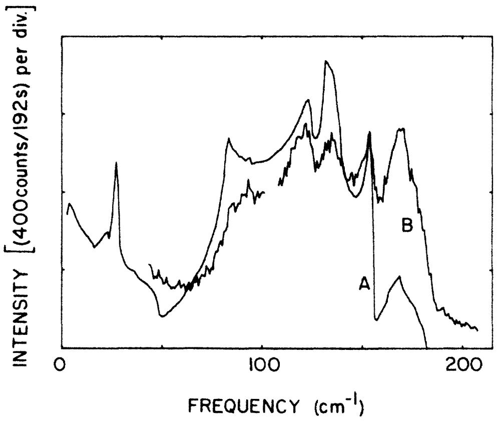

FIG. 3. Comparison of computed and measured Raman spectra. The polycrystalline-weighted average of Fig. 2 has been scaled in frequency by a factor of 1.193 (A) for comparison with the spectrum obtained from the crystal grown at 10 kbar and cooled at 12 K (B). Further, the two spectra have been normalized at the peak arising from W_{2L}. All predicted features are evident in the measured spectrum; however, the relative intensities of the observed features are not in good agreement with those predicted by the point-dipole model.

scale for comparing the observed and calculated spectra. If the contribution from S_{11} is lessened in an attempt to correct the strength at L_{2T}, the increased contribution from S_{44} will further aggravate the disagreement at L_{L+T} and J_{2L}. Assuming that the correct density of states (as provided by lattice-dynamics theory) was used as a basis for the calculated spectrum, fault probably lies with the model used for calculating the polarizability. Inasmuch as the feature labeled L_{L+T} is the only one in which phonons are mixed from different branches, it may be concluded that the coupling between phonons of different branches has been exaggerated in the point-dipole model used in the calculation. Further, the intensity at J_{2L} is about a factor of 3 larger than expected. It appears that the coupling between longitudinal phonons, relative to that between transverse ones, has been underestimated by the point-dipole model. The discrepancy most likely worsens for the heavier rare-gas solids. As pointed out by Leese *et al.*,[10] overlap of the atomic wave functions is neglected in this model. The longitudinal phonons cause the atoms to "bump" each other harder than for transverse phonons; a shell model may be useful in improving the polarizability weighting.

TEMPERATURE EFFECTS

The temperature dependence of the spectra is shown in Fig. 4 for temperatures from 0.1 to 2 times the Debye temperature, 120 K for the 10-bar crystal. As the temperature was increased, the sharp cutoff at twice the maximum lattice frequency was relaxed and the sharp features of the spectra became obscured because the phonon lifetimes were shortened through phonon interactions. Above the Debye temperature, the only remaining feature was due to the lowest-frequency two-phonon critical point L, which arises from a pair of transverse phonons at the zone boundary. The low-frequency part of the spectrum becomes filled in as the temperature is increased because these phonon pairs are becoming highly populated. With the simplifying assumption that all pairs contributing to Raman scattering are from the same branch, the effects of phonon occupation may be removed from the spectra by dividing by $[n(\omega/2)+1]^2$, where $n(\omega)$ is the phonon occupation number $[\exp(h\omega/kT)-1]^{-1}$. It can be seen in Fig. 5 that the resulting thermally depopulated spectra maintain about the same intensity and overall shape. The smoothing of the features as the temperature approaches Θ_D is apparent. The variation of spectral intensity and shape from low temperature to near melting can thus be ascribed to the changing occupation number of the phonon pairs and smoothing of the joint density of states as the temperature rises.

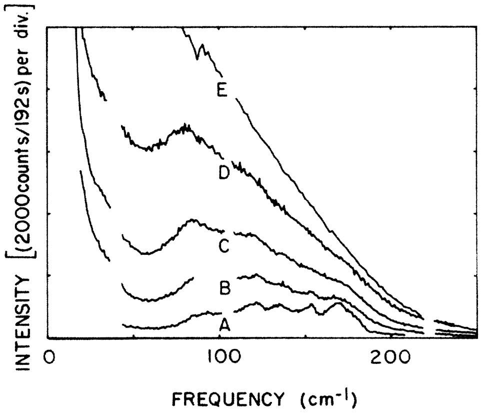

FIG. 4. Temperature dependence of second-order Raman spectra. Spectra A, B, C, D, and E were obtained from the crystals grown at 10 kbar and cooled at 12, 80, 118, 180, and 242 K, respectively. As the temperature is increased, the Raman intensity grows and the sharp features becomes obscured. The last feature to survive arises from the lowest-frequency phonons at the zone edge, L_{2T}.

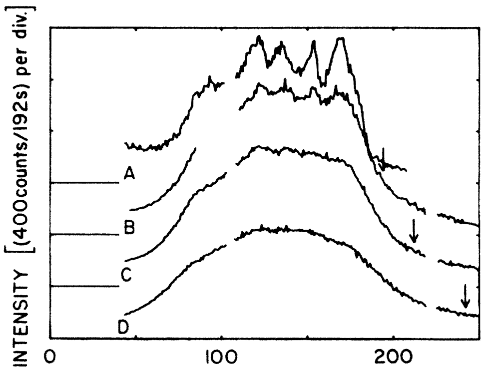

FIG. 5. Thermally depopulated spectra of solid argon. The effect of phonon occupation has been approximately removed from the spectra shown in Fig. 4 by division by $[n(\omega/)+1]^2$, where $n(\omega)=[\exp(\hbar\omega/kt)-1]^{-1}$. Each subsequent spectrum is offset vertically by one division. The arrows indicate the predicted positions of two-phonon bound-state features.

In principle, detailed information about the temperature dependence of the linewidth of the various phonons can be obtained by deconvolving a high-temperature spectrum by a "0-K" spectrum after removing the spectrometer response. Caution should be exercised, however, in interpreting the thermally depopulated spectra below 80 cm^{-1} since phonon difference processes contribute with a different temperature dependence. Also the thermal depopulation suggested above will not be accurate if there is significant spectral contribution from pairs of phonons from different branches having significantly different energies.

The theoretical possibility of two-phonon bound states in rare-gas solids has previously been raised.[11] Jindal and Pathak have predicted that at sufficiently high temperatures, a spectral feature should develop above the two-phonon cutoff at $2\omega_D$ and increase linearly in frequency with increasing temperature. The expected intensity of the feature has been estimated to be comparable to that of the two-phonon Raman spectrum.[12] Figure 5 shows the predicted position of this feature—no evidence for the bound state was found. The question of a bound state in rare-gas solids awaits a renewed theoretical investigation.

TABLE I. Comparison of phonon frequencies at various critical points for crystals grown at 5 kbar (A) and 10 kbar (B) and cooled at 12 K.

Critical Point	Frequency (cm^{-1}) A	B	Ratio
L_{2T}	69.7	83.1	1.19(2)
W_{2T}	100.4	120.8	1.20(3)
L_{L+T}	112.5	134.5	1.19(6)
W_{2L}	126.9	152.9	1.20(5)
J_{2L}	139.0	168.6	1.21(3)
L_{2L}	154.4	186.9	1.21(0)

DENSITY EFFECTS

The phonon frequencies observed in the two crystals at 12 K are summarized in Table I. The overall fractional increase in phonon energy from the crystal grown at 5 kbar to the one grown at 10 kbar was slightly more than 20%. While there was a tendency for the longitudinal phonons to exhibit a slightly larger shift with density than the transverse phonons, this difference is within our experimental uncertainty. More accurate determination of mode-dependent variation of pressure shifts will require further measurement.

The crystals are clamped at nearly constant volume by the pressure cell as they are cooled from the freezing temperature. Both elastic contraction of the cell as the sample pressure drops upon cooling and thermal contraction of the cell contribute to an increase of sample density on cooling to 12 K. A formulation of these corrections has been established elsewhere.[13] The corrections to sample density were found to be 5.6% and 6.0% for the samples grown at 5 and 10 kbar, respectively. That is, the crystal grown at 20.61 $\mathrm{cm}^3/\mathrm{mol}$ (10.0 kbar) had a density of 19.4 $\mathrm{cm}^3/\mathrm{mol}$ (7.4 kbar) at 12 K. The lower-density crystal grown at 22.05 $\mathrm{cm}^3\mathrm{mol}$ (5.0 kbar) changed to 20.8 $\mathrm{cm}^3/\mathrm{mol}$ (3.1 kbar) on cooling.

The density dependence of phonon frequencies is commonly represented by the mode Grüneisen parameter, $\gamma = -\partial \ln(\omega)/\partial \ln(V)$. The overall Grüneisen parameter measured for the crystals at 12 K was found to be 2.67 ± 0.05, from the ratio of frequencies 1.203 and the ratio of volumes 0.933. This compares favorably with the value of 2.65 reported for the thermodynamic Grüneisen parameter.[14] A direct measure of the internal cell pressure will provide a more accurate determination of the mode Grüneisen parameters and their pressure dependencies.

The overall mode Grüneisen parameter at a higher temperature was determined from the thermally depopulated spectra obtained from the crystals near melting. Although the crystal density was known more accurately near the melting line, a larger uncertainty is assigned to this Grüneisen parameter since the detailed effects of removing the phonon occupation from the spectra are unknown. It was found that a fractional frequency increase of 17.7% was required to map the spectrum of the 5-kbar crystal onto the spectrum of the 10-kbar crystal, corresponding to a Grüneisen parameter of 2.4 ± 0.1. This is in disagreement with the expectation that the high-temperature Grüneisen parameter is slightly higher than the low-temperature value[15] and could indicate a problem with our simplified procedure for thermal depopulation.

MELTING

The spectrum of the fluid just after melting was also studied at 5 and 10 kbar. The integrated intensity of the fluid spectrum is about ten times that of the solid. The semilogarithmic plot shown in Fig. 6 clearly shows the nearly exponential spectrum of the fluid and the much greater intensity at low frequencies. At atmospheric pressure, the high-frequency parts (short-time dynamics) of the solid and fluid spectra have been shown to be similar.[6] Comparison of the high-frequency spectral tails has been extended here since the intensities have been measured an additional order of magnitude lower than previously reported. At high pressure, the similarity between the solid and fluid tails becomes less striking and if the solid spectra is scaled to represent the fluid density via the Grüneisen parameter mentioned above, the similarity between the two spectra is reduced even further.

Can the fluid spectrum be attributed to second-order scattering from phononlike excitations? The thermal depopulation of phonon occupation, successful for the solid spectra, was applied to the fluid spectra. The thermally depopulated fluid spectra exhibited a "peak" that was twice as large as the solid spectra. Further, the peak was shifted to a lower frequency by an amount which would require a Grüneisen parameter three times that measured. Although it was expected that severely overdamped phonons would shift to lower frequency, the increased intensity cannot be explained by a second-order process invoking phonons in the fluid but could arise from disorder-induced first-order scattering[16]

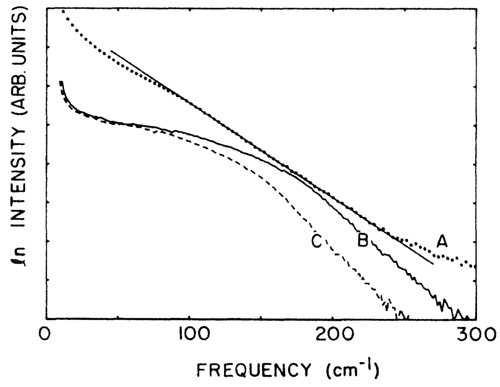

FIG. 6. Comparison of spectra of solid and fluid argon near melting. A semilogarithmic plot of the fluid argon spectrum (A), 21,8 $\mathrm{cm}^3/\mathrm{mol}$ at 10 kbar and 256 K, shows its nearly exponential character, with a characteristic decay frequency of 41 cm^{-1}. The solid spectrum (B), 20.6 $\mathrm{cm}^3/\mathrm{mol}$ at 10 kbar and 242 K, shows a tenfold decrease in intensity at low frequency. When adjusted to the fluid density via the Grüneisen parameter, the solid spectrum (C) shows a 35% faster decay at high frequency than the fluid spectrum.

(which could also explain the large shift to lower frequency). A more reasonable approach for comparing the solid and fluid spectra might come from applying fluid considerations to the solid, such as scattering induced by collisions between pairs of atoms.

SUMMARY

The Raman spectra obtained from high-density argon crystals can provide information about the dynamics, anharmonic effects, and contributions to polarizability of the phonons. We have found that discrepancies exist between the relative intensities of the spectral features and those predicted by a point-dipole model. In addition, a bound state predicted in argon was not observed. A detailed understanding of the differences between the solid and fluid spectra observed near melting is not yet available. Questions concerning condensed argon still remain for theoretical and simulation investigations. Detailed observations of the pressure and temperature dependence of phonon energies and lifetimes may be obtained through more exacting measurement as theoretical interest warrants.

ACKNOWLEDGMENTS

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