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Polarized Raman spectra of silver halide crystals[*][†]

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Second-order Raman spectra of AgCl and AgBr single crystals have been measured at 77 K. By using oriented crystals and different polarizations of the incident and scattered light the separate contributions of Γ_1, Γ_{12}, and $\Gamma_{25'}$ symmetries are determined for the first time in these materials. These data are compared with calculated two-phonon dispersion curves. A few van Hove singularities are identified and the relative contribution of different branches inferred. The longitudinal-optic-phonon-overtone (2LO) peak shows significant quasiresonant enhancement for the argon-laser lines used.

I. INTRODUCTION

The vibrational properties of silver halide crystals have received little attention in comparison to alkali halides. It is only in the last few years that experiments have been done[1] and theories developed[2] which suggest that there may be significant qualitative differences in the lattice dynamics of the silver halides. In particular, Fischer *et al.*[2] have proposed that there will be several significant differences because of the deformability of the *d* shell of the Ag^+ ion and because of the partially covalent bonding in the silver halides. The discussion so far has been based on one piece of experimental evidence, the phonon dispersion curves measured for AgCl using inelastic neutron scattering.[1] A more sensitive test of the predicted differences should be possible, at least in principle, by studying second-order Raman scattering in the silver halides. This paper presents the first polarized second-order Raman spectra for oriented single crystals of AgCl and AgBr.

First-order Raman scattering is forbidden in crystals of O_h symmetry because each ion is at a center of inversion. The allowed second-order scattering is a measure of the two-phonon density of states weighted by the contribution of each phonon pair to the Raman scattering tensor. In crystals of O_h symmetry this tensor has three independent components (of symmetry Γ_1, Γ_{12}, and $\Gamma_{25'}$) and these may be studied separately by appropriate choices of polarization and crystal orientation.[3] These weighted densities of states for each symmetry component should be quite sensitive to different assumptions for the phonon eigenvectors and their contribution to the polarizability of the crystal.[4,5]

The only previous Raman spectra reported for these crystals were measured with unoriented samples at low resolution.[6] Measurements with higher resolution for other compounds have tended to emphasize the comparison with phonon eigenfrequencies.[7] In principle, from an analysis of van Hove singularities in the polarized second order spectra, it should be possible to determine two-phonon critical point frequencies. However, in practice, the number of these critical points is so large and they are so poorly resolved in presently available spectra that only a very few convincing assignments are possible. The data presented here suffer from the same limitation so a detailed critical-point analysis will not be attempted. However, since little other experimental information on phonon dispersion is available for AgBr, an attempt will be made to identify a few critical frequencies to compare with Fischer's predictions. A comparison with his calculated two-phonon dispersion curves will also be used to determine which modes make the dominant contribution to the Raman scattering.

Finally, the apparent quasiresonant enhancement of the 2LO-phonon scattering when the laser is near the indirect band edge will be discussed. This is an interesting effect in its own right, but somewhat complicates the comparison of these data with the lattice dynamics theory.

II. EXPERIMENTAL

Single crystals of pure AgCl and AgBr were obtained from three different sources: Kodak Research Laboratories in Rochester, the Crystal Growing Facility of the University of North Carolina in Chapel Hill, and the Institute of Physical Chemistry of the Bulgarian Academy of Sciences in Sofia. Unpolarized Raman spectra in these crystals did not show any important differences. The polarized spectra presented in this paper were studied using the samples obtained from the University of North Carolina.[8]

The crystals were oriented and then rectangular samples were cut and polished and etched to dimensions of a few millimeters on a side. The final samples had two {110} and one {100} faces whose orientation was checked using Laue x-ray

TABLE I. Scattering configurations used to measure the polarized spectra.

Standard notation	Polarization of incident light	Polarization of scattered light	Elements of the polarizability tensor
$z(x, x)y$	$[1\bar{1}0]$	$[1\bar{1}0]$	$\lvert\alpha_1\rvert^2+\frac{1}{3}\lvert\alpha_{12}\rvert^2+\lvert\alpha_{25'}\rvert^2$
$z(x, z)y$	$[1\bar{1}0]$	$[110]$	$\lvert\alpha_{12}\rvert^2$
$z(y, x)y$	$[001]$	$[1\bar{1}0]$	$\lvert\alpha_{25'}\rvert^2$
$z(y, z)y$	$[001]$	$[110]$	$\lvert\alpha_{25'}\rvert^2$

photographs and found to be accurate to within 1° or 2°.

Raman spectra were measured for the incident and scattered polarizations listed in Table I. The spectrometer incorporated a 2-W cw argon-ion laser, a Spex 1401 double monochromator, and photon counting detection. The spectra were measured with an instrumental slit width of 1.7 cm^{-1} and a wave-number accuracy of better than ± 2 cm^{-1}. Polarized spectra were corrected for the polarization dependence of the instrument response.

Using any of the argon-laser lines to excite the Raman spectra in AgCl, at 77 K a broad emission band was observed as a more or less disturbing background. Although the excitation mechanism of this emission is not understood the position of its maximum suggests that it is due to the radiative exciton decay that is known to give a luminescence band at about 4900 Å. The emission band was found to be least disturbing for 5145-Å excitation and this line was used for AgCl. A constant background (30–60% of the strongest peak) was subtracted from the data to correct for this emission. The statistical uncertainty in the resultant Raman intensity was a few percent of the peak heights.

In AgBr, the 4880-Å laser line was chosen. Only a small (2%) background correction was needed in this case. Excitation at shorter wavelengths produced strong recombination luminescence, while excitation in some crystals produced another broad emission band (peaking at 5250 Å) known to be due to I^- impurity present in small amounts in the purest crystals available.[9] At helium temperature the intensity of this I^- emission increases, it shifts to the blue, and detailed structure appears, so a study of Raman scattering at lower temperatures was not undertaken.

III. RESULTS AND DISCUSSION

The Raman spectra of AgCl and AgBr obtained at 77 K are shown in Figs. 1 and 2 for different polarizations of the incident and scattered light. For AgBr, both the anti-Stokes and Stokes spectra are shown. In each figure, (a) represents the $z(x, x)y$ spectrum containing Γ_1, Γ_{12}, and $\Gamma_{25'}$ contributions, while (b), (c), and (d) show each of these contributions separately on the same relative scale. Curves for (b) and (c) were measured in $z(x, z)y$ and $z(y, x)y$ geometries, respectively, while (d) was obtained by subtracting (c) and one-third of (b) from (a) to get the Γ_1 contribution. The $\Gamma_{25'}$ spectrum was also verified using the $z(y, z)y$ geometry. No additional check of the Γ_1 spectrum was made since this would have required a different crystal orientation.

The Raman spectra of AgCl and AgBr are similar with regard to the relative spectral positions and the polarizations of the prominent features. There seem to be three characteristic regions in the

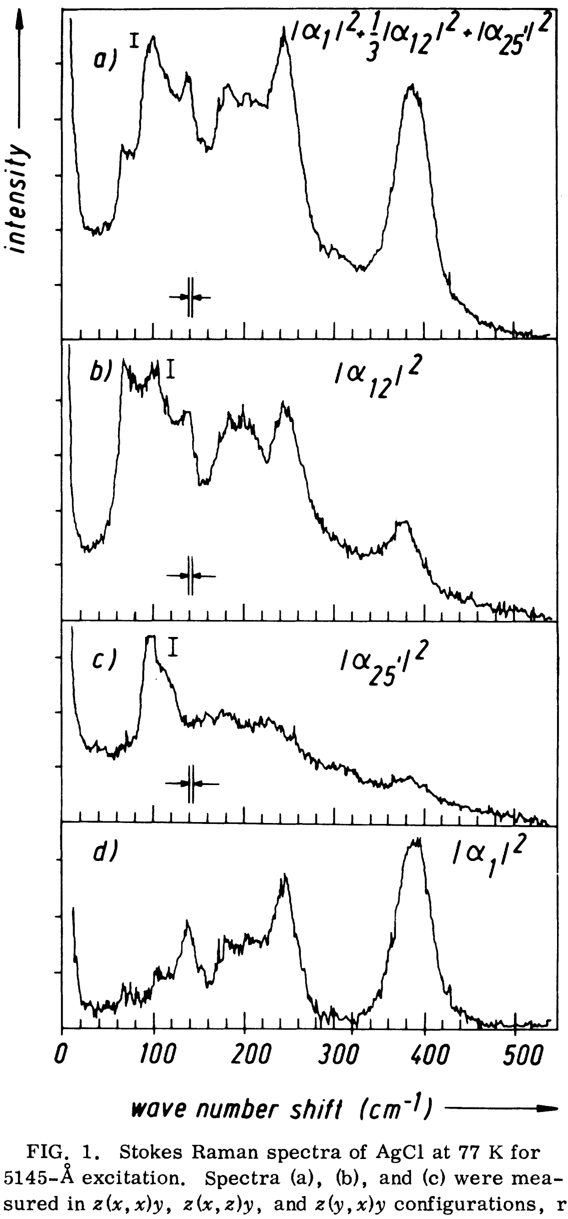

FIG. 1. Stokes Raman spectra of AgCl at 77 K for 5145-Å excitation. Spectra (a), (b), and (c) were measured in $z(x,x)y$, $z(x,z)y$, and $z(y,x)y$ configurations, respectively. Spectrum (d) is the Γ_1 spectrum computed from (a) $-\frac{1}{3}$ (b) $-$ (c).

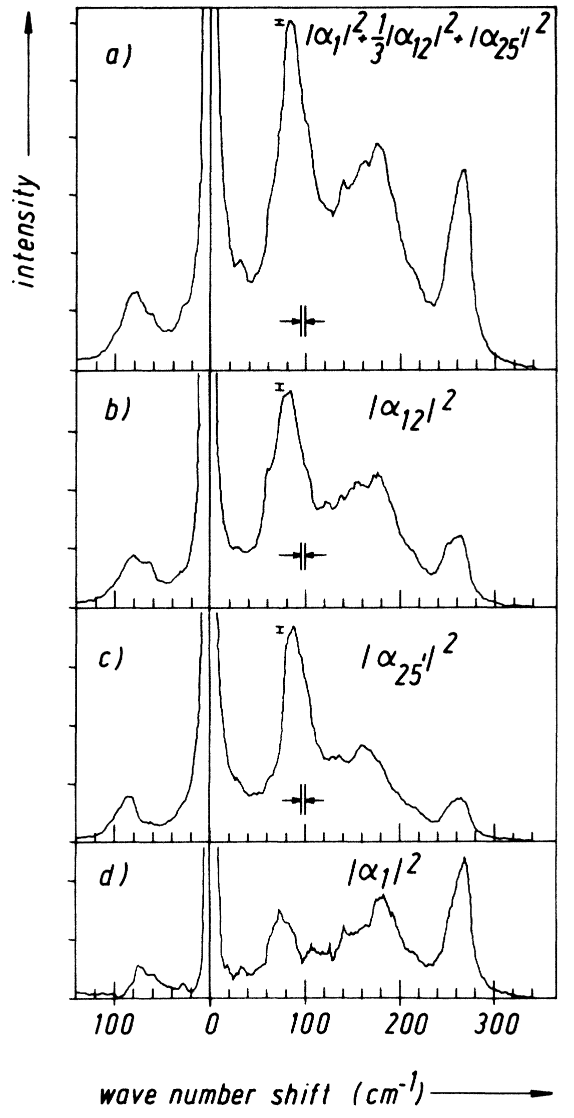

FIG. 2. Stokes and anti-Stokes Raman spectra of AgBr at 77 K for 4880-Å excitation. (See Fig. 1 caption for details.)

spectra which can be identified by comparison with the two-phonon dispersion curves determined from neutron scattering[1] and from calculations by Fischer *et al.*[2] and shown in Figs. 3 and 4.

One is the strong structured peak in the range 60–150 cm^{-1} in AgCl and 40–110 cm^{-1} in AgBr. This can be assigned to processes involving two acoustic phonons. The expected M_1 saddle point at the lowest critical wave number [2TA(X)] can be observed at its predicted position (66 cm^{-1} in AgCl and 60 cm^{-1} in AgBr). Other singularities are less certain. Possible assignments are listed in Table II for those cases where the same singularity is seen in both crystals.

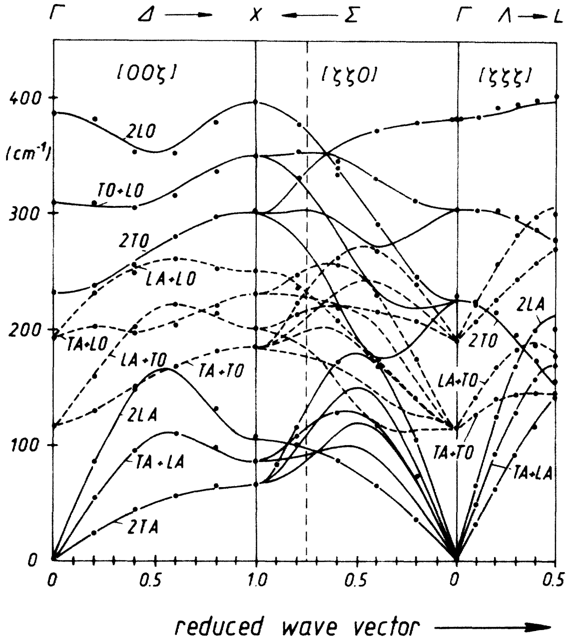

FIG. 3. Two-phonon dispersion curves for AgCl at 77 K. Experimental data (points) and theoretical fits (lines) are taken from Ref. 1 except for the transverse branches TA$_2$ and TO$_2$ along Λ that were taken from Ref. 2.

The second region, from 150–280 cm^{-1} in AgCl and 110–200 cm^{-1} in AgBr, has less pronounced structure. Combinations of optic and acoustic phonons appear to make the dominant contribution. The strongest peak (at 250 cm^{-1} in AgCl and 180

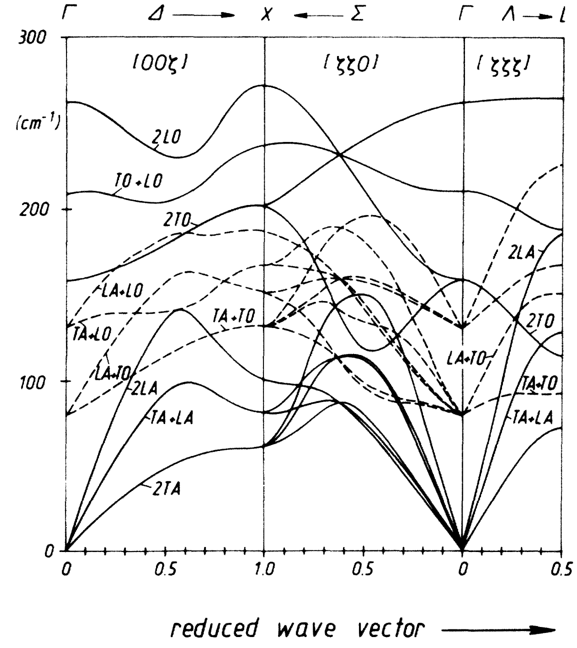

FIG. 4. Two-phonon dispersion curves for AgBr based on computed curves in Ref. 2.

TABLE II. Possible assignments for some of the dominant features in acoustic region.

Symmetry	Assignment	Predicted wave number (cm^{-1}) AgCl	AgBr
Γ_1	2TA(L)	143	74
Γ_{12}	2TA(X)	66	62
	$\mathrm{TA}_1+\mathrm{TA}_2(\Sigma)$	101	89
$\Gamma_{25'}$	TA + LA(X)	88	82
	$\mathrm{TA}_1+\mathrm{TA}_2(\Sigma)$	101	89

cm^{-1} in AgBr) appears to come at least in part from LA + LO(Δ).

The third region, from 280–420 cm^{-1} in AgCl and from 200–300 cm^{-1} in AgBr, contains a single broad peak which is strongest in the Γ_1 spectra. This peak, at ~390 and 265 cm^{-1}, respectively, is clearly associated with the 2LO branch. The broad valley at ~300 and 200 cm^{-1}, respectively, indicates that the LO + TO branch and the 2TO branch make only weak contributions to the spectra.

The prominence of the 2LO peak was also noted by Bottger and Damsgard.[6] They found that it increased in intensity several fold relative to the other features as they changed from 6471- to 4579-Å laser excitation. This increase was also noted for the more limited range of laser frequencies used in this experiment. In Fig. 5 the unpolarized 2LO peak of an unoriented AgBr crystal at 77 K is shown for different exciting wavelengths. The spectra were normalized to the peak at 82 cm^{-1} and show an increase of about 20% in this range.

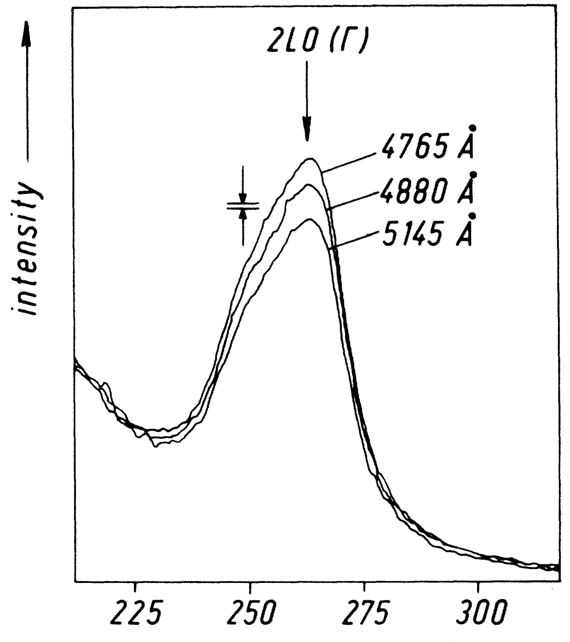

FIG. 5. Raman scattering in the 2LO peak of AgBr at 77 K for different excitation wavelengths. The spectra are unpolarized and were normalized to the peak intensity at 82 cm^{-1} (not shown). The arrow indicates the position of 2LO(Γ) calculated in Ref. 2.

This increase and the prominence of the 2LO peak are reminiscent of the onset of resonant LO phonon scattering near the direct exciton edge observed already in many crystals.[10,11]

In the silver halides the optical absorption shows a low-energy tail that is explained in terms of indirect exciton transitions, with a threshold for indirect absorption at about 3840 and 4650 Å in AgCl and AgBr.[12] The direct exciton edge is at about 2407 and 2890 Å, respectively.[13] In a previous study of an indirect gap crystal (GaP), Scott *et al.*[14] found that the resonant enhancement is associated with the direct exciton and not the indirect exciton. The 2LO enhancement in the silver halides appears to be consistent with this, but it will be necessary to investigate the behavior closer to the direct exciton edge to be sure.

The peak in Fig. 5 appears to be centered at the predicted 2LO(Γ) wave number of 263 cm^{-1}, as expected for coupling of the exciton with long-wavelength phonons.[15] However, the 2LO peak in both AgCl and AgBr shows additional structure. Broadening of the two-phonon contribution is partly responsible for the width of the peak, and for the fact that it has a tail extending beyond twice the maxi-

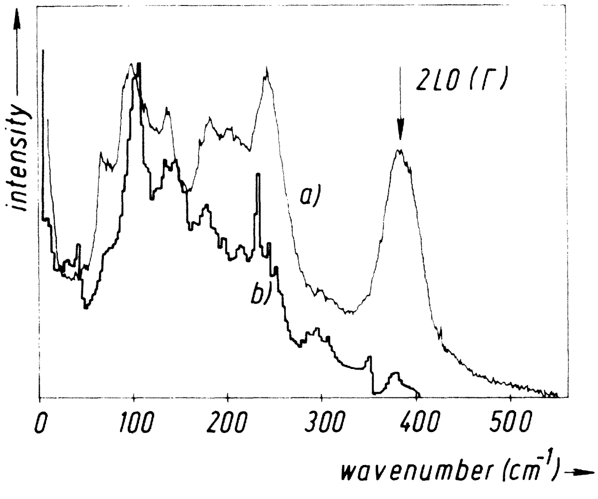

FIG. 6. (a) Measured and (b) computed Raman spectra for AgCl at 77 K. Curve (a) is an unpolarized spectrum [(a) + (b) in Fig. 1]. Curve (b) is taken from Ref. 2. The arrow indicates the position of 2LO(Γ) based on the neutron measurements of Ref. 1.

mum phonon frequency. But it appears that 2LO processes from other parts of the Brillouin zone may also be contributing.

Because of the enhancement of the 2LO peak one must be cautious about comparing the spectra with computed line shapes. Such line shapes for Γ_1, Γ_{12}, and $\Gamma_{25'}$ contributions separately are not yet available. However, a comparison with two-phonon densities of states is instructive since this corresponds to the assumption that each phonon pair makes the same contribution to the polarizability. Figure 6 shows a spectrum computed in this way for AgCl (including both sum and difference processes at 77 K) and the corresponding experimental spectrum. The experimental curve for all modes ($|\alpha_1|^2 + \frac{4}{3}|\alpha_{12}|^2 + |\alpha_{25'}|^2$) was obtained according to Table I by adding curves (a) and (b) in Fig. 1. While the positions of the features agree fairly well, it is clear that there are large discrepancies in the intensities, indicating that different phonon pairs contribute differently to the polarizability. Further discussion of these discrepancies must await the calculation of spectral densities for the separate symmetry components.

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