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Reply to "Comments on 'Theoretical study of impurity-induced first-order Raman spectra for the alkali halides'"*

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This is a reply to the preceding comment by Page on the relative merits of the breathing-shell and deformation-dipole models for predicting defect-activated first-order Raman spectra. We show that when both models are parametrized in the same fashion the agreement between theory and experiment is comparable.

The preceding paper[1] is concerned with our recent paper[2] in which we presented the results of calculations, based on the deformation-dipole model (DDM), for the E_g components of the first-order Raman spectra of KCl, KBr, KI, and RbCl doped with Tl^+. In that paper we compared our results with those obtained by Harley, Page, and Walker[3] using the breathing-shell model (BSM) and attributed the discrepancies between the two to the fact that the BSM had been "fitted to known dispersion curves" while the DDM was not so adjusted.

In his paper Page is concerned that by this statement we might have been implying that a large number of parameters (e.g., 11) had been used. This was not our intention, but the fact remains that the monopole charge Z was used as a fitting parameter, at least for KI and KBr. In this sense information from the dispersion curves has been employed and the Harley-Page-Walker (HPW) calculations are not based *solely* on macroscopic input data. Previously we held Z fixed at unity, the value indicated by the highly ionic character of the bonding in alkali halides and most consistent with the observed cohesive energies.[4] Any model which one uses for the dynamics should be reasonably consistent with the interpretation of these static properties and it appears to us that models with $Z = 0.9$, which imply 10% covalent bonding do not satisfy this requirement and should be regarded as parametrized to fit the dynamical data.

Recently, we have obtained new results for the E_g spectra[5] calculated using DDM phonons derived from a model which was identical with that used earlier[2] *except* that instead of holding Z fixed at unity we used values of Z which were adjusted to optimize the fit to the measured dispersion curves. These are thus directly comparable with the HPW results since both models (DDM and BSM) are now parametrized in the same way. The only difference is that the elastic constants are not used as input data in the DDM calculations.

The results for KBr are shown in Fig. 1 and for KI in Fig. 2. In each case the corresponding results for $Z = 1$ are also shown for purposes of comparison.

It can readily be seen that the new results are very close to the HPW results as far as the acoustic regions of the spectra are concerned and possibly in a little better agreement with experiment, in that the DDM spectra show a somewhat sharper rise on the low-frequency side of the first major peak.

In the optic regions of the spectra there is more dissimilarity; specifically the DDM results show a small but sharp peak at about 130 cm^{-1} for KBr and at about 115 cm^{-1} for KI. These are not present in the BSM spectra, however, it is interesting to observe that in each case there is a corresponding peak in the experimental spectrum, although it is significantly stronger and broader.

On the basis of the present results it would appear that, at least for KBr and KI, there is little to choose between the two models (BSM and DDM) when both are *parametrized to fit the measured dispersion curves in the same manner.*

As regards the other two crystals treated by HPW (KCl and RbCl) reducing Z in the DDM calculations does not improve the agreement between our results and the HPW results as far as the theoretical unperturbed E_g spectra are concerned. However, since HPW found that it was necessary to modify the defect nearest-neighbor force constants significantly in order to obtain fits to the observed spectra, it is quite possible that perturbed densities of states derived in the same way from our unperturbed spectral densities could give agreement which is at least as good as that which they obtained. This is particularly likely for KCl since our unperturbed E_g spectrum shows peaks at, or close to, those present in the experimental spectrum including a sharp peak close to 160 cm^{-1}, which is enhanced when Z is reduced to fit the measured dispersion curves. This last feature is

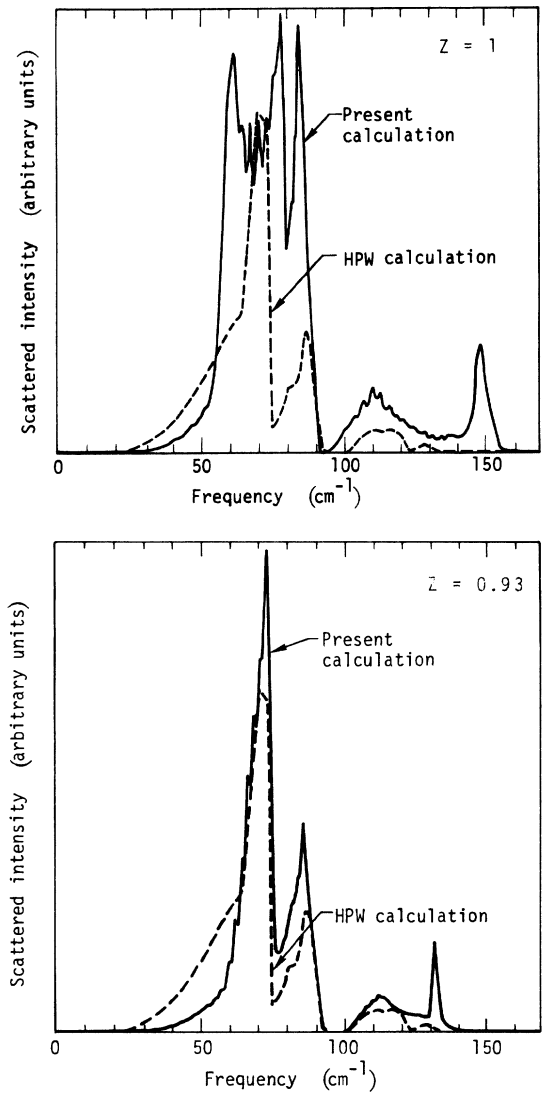

FIG. 1. Theoretical E_g components of the defect-activated Raman spectrum for KBr, assuming no force constant changes for a substitutional monovalent impurity at the K^+ ion site.

absent from the BSM spectra. Thus, since HPW found that a change in the defect nearest-neighbor force constants could be used to vary relative peak strengths without significantly shifting their positions, it is possible that the DDM phonons could give a better reproduction of the experimental spectrum.

As far as RbCl is concerned the experimental spectrum is dominated by a single sharp peak due to a strong in-band resonance close to the low-frequency cutoff of the optic modes. We could certainly obtain such a resonance using the DDM E_g spectral function with perturbed defect–first-neighbor force constants since our spectrum is very similar in shape to the BSM spectrum in this region. The only major difference is a bodily displacement of the whole spectrum by ~ 10 cm^{-1} to higher frequencies. Thus, one would expect the predicted resonance to be similarly shifted which would put it on the high-frequency side of the observed peak by about 5 cm^{-1}, since the BSM results give a peak whose frequency is 5 cm^{-1} too low. If this were the case then the DDM and BSM results would agree equally well with experiment. Whether the small high-frequency side band would also be reproduced is harder to say. However, it would appear that, since the resonance dominates the observed spectrum, the latter is only sensitive to the properties of the normal modes whose fre-

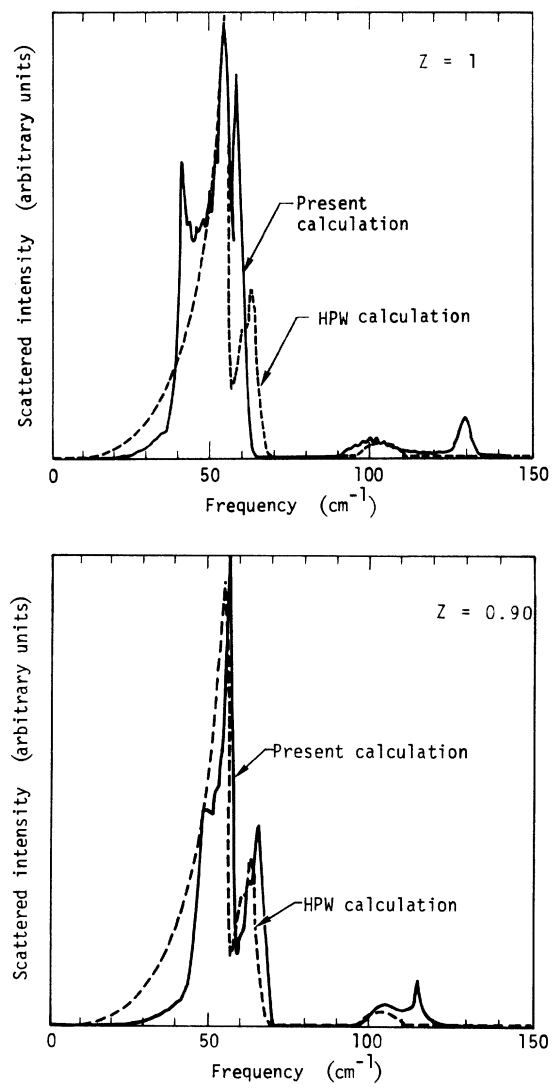

FIG. 2. Theoretical E_g components of the defect-activated Raman spectrum for KI, assuming no force constant changes for a substitutional monovalent impurity at the K^+ ion site.

quencies lie in the neighborhood of the resonance. Since both BSM and DDM spectra are very similar in this region (a similarity which remains even when Z is varied in the DDM calculations), the observed spectrum does not discriminate between them.

On the basis of these last considerations it would appear likely that our contention that DDM calculations are at least as good as comparable BSM calculations is also valid for KCl and RbCl.

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[1]J. B. Page, Jr., preceding paper, Phys. Rev. B 13, 4630 (1976).

[2]A. M. Karo and J. R. Hardy, Phys. Rev. B 12, 690 (1975).

[3]R. T. Harley, J. B. Page, Jr., and C. T. Walker, Phys. Rev. B 3, 1365 (1971).

[4]M. P. Tosi, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. 16, p. 1.

[5]A. M. Karo and J. R. Hardy, *Proceedings of the Third International Conference on Light Scattering in Solids*, edited by M. K. Balkanski, R. C. C. Leite, and S. P. S. Porto (Flammarion, Paris, to be published).