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

John B. Page, Jr.

*Department of Physics, University of Utah, Salt Lake City, Utah 84112
and Department of Physics, Arizona State University, Tempe, Arizona 85281* †

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A recent paper of Karo and Hardy is discussed with regard to the comparison of calculated projected densities of states for defect-phonon calculations based upon different models for the host-crystal phonons.

In a recent paper,[1] Karo and Hardy presented theoretical $E_g$ components of the first-order Raman spectra associated with positive monovalent impurities in KCl, KBr, KI, and RbCl for the case of unperturbed force constants and nonzero electronic polarizability derivatives on the defect's six nearest neighbors. Since the $E_g$ modes involve no defect motion, these spectra are independent of the defect mass, and their frequency dependence is determined solely by the host-crystal phonons. Karo and Hardy's calculated spectra were based upon deformation-dipole-model[2] (DDM) phonons and were compared with analogous calculations, based upon breathing-shell-model[3] (BSM) phonons and carried out by Harley, Page, and Walker[4] (HPW) in a study of Raman scattering from $Tl^+$-doped KCl, KBr, KI, and RbCl. In the latter work, it was shown that good agreement with the experimental $E_g$ spectra is obtainable for unperturbed, or in the case of $KCl:Tl^+$ and $RbCl:Tl^+$, weakly perturbed phonons (for these two crystals the change in the defect-nearest-neighbor longitudinal overlap force constant was found to be 0.1 and $-0.1$, respectively). The experimental $E_g$ spectrum for $KBr:Tl^+$ and the corresponding calculated BSM spectrum of HPW are shown in Fig. 1(a).[5,6] For comparison, the corresponding calculated DDM spectrum of Ref. 1 is shown in Fig. 1(b), and it is seen to be in poor agreement with both the experimental spectrum and the calculated BSM spectrum. The calculated spectra of Fig. 1 differ only in the unperturbed phonons used. In Ref. 1 it is shown that similar discrepancies between the calculated unperturbed DDM and BSM $E_g$ spectra occur for the cases of KI, KCl, and RbCl hosts as well, with the discrepancies being somewhat worse for KBr and RbCl than for KCl and KI. Karo and Hardy[1] attribute the discrepancies to "the fact that the deformation-dipole models were not adjusted to fit the measured dispersion curves," whereas the HPW calculations "used breathing-shell models fitted to known phonon dispersion curves." It is the purpose of this note to point out that the latter statement concerning the breathing-shell model used in HPW is perhaps

misleading, in that it could be interpreted to mean that the BSM phonons used by HPW were obtained from a multiparameter fit to the measured dispersion curves, such as the eleven-parameter fit for KI carried out by Dolling et al.[7] using the shell model.

Such was not the case. As was emphasized in HPW, the BSM employed there used input parameters obtained from macroscopic data such as elastic constants, dielectric properties, etc. In-
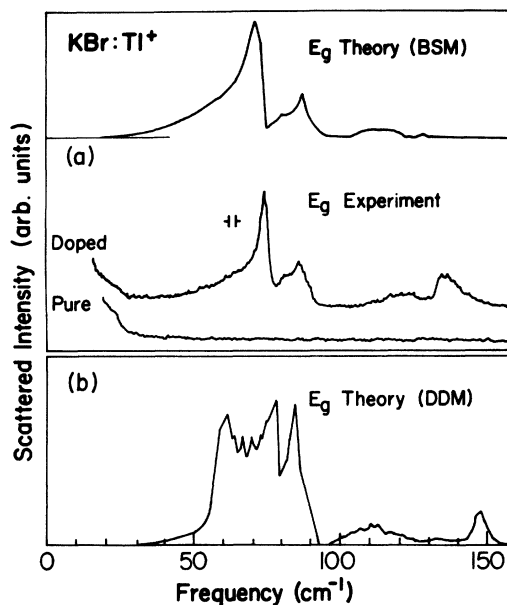


FIG. 1. (a) Experimental and theoretical $E_g$ Raman spectra of Ref. 4, for KBr: $Tl^+$. The temperature of the experiments was 15 °K and the instrumental gain was the same for both the doped and the pure crystals. The theoretical curve is for zero force–constant change and was computed using 0 °K BSM phonons obtained from macroscopic data as described in the text. It has been normalized to reflect the experimental intensity. (b) Theoretical $E_g$ Raman spectra of Ref. 1, for a positive monovalent impurity in KBr. This curve is for zero force-constant change and 0 °K, and it was computed using DDM phonons. It has been normalized to reflect the experimental intensity.

deed, the input parameters used by HPW for the $T = 0$ BSM phonons of RbCl are given in Table II of their paper, and there one sees that these parameters consist of the elastic constants $c_{11}$, $c_{12}$, $c_{44}$; dielectric constants $\epsilon_0$, $\epsilon_\infty$; reststrahlen frequency $\omega_0$; ionic polarizabilities $\alpha_+$, $\alpha_-$; nearest-neighbor distance $r_0$; and atomic masses $m_+$, $m_-$. In addition to these quantities, one needs only the value of the ionic change $Z$, and in all of the BSM calculations of HPW, $Z$ was kept fixed at $Z = 0.9$. This value was previously shown by Schröder to lead to good agreement with the measured dispersion curves of KI, KBr, NaI, and NaF.[8] Thus only in the sense of the single input parameter $Z$ could the BSM phonons be claimed to have been fitted, and then only for the four crystals listed above.

One of the aims of HPW was to compare calculated Raman spectra based upon shell-model phonons obtained from a multiparameter fit to measured dispersion curves with calculated spectra based upon BSM phonons obtained from macroscopic input data as listed above (keeping $Z = 0.9$). HPW made this comparison for KCl and KBr, and the calculated spectra were in very close agreement. Thus the eigenvectors as well as frequencies provided by these two models are in close agreement, at least insofar as the eigenvector sums over the Brillouin zone involved in computing the Raman spectra are concerned. This, together with the good agreement between theory and experiment obtained by HPW using BSM phonons points up the usefulness of the BSM, for which measured dispersion curves are unnecessary.

In view of the fact that the BSM phonons used in the calculations of HPW were based upon macroscopic input data, as were the DDM phonons used by Karo and Hardy in Ref. 1, it would seem that the lack of agreement between the calculated spectra of Ref. 1 and the experimental and calculated BSM spectra of HPW arises from inadequacies in the version of the DDM used in Ref. 1. It is interesting to note that unperturbed nearest-neighbor $E_g$ spectra for Tl$^+$-doped KCl, KBr, and KI calculated by Benedek and Terzi,[9] using DDM phonons that *have* been fit to measured dispersion curves are in quite good agreement with the BSM calculations of HPW.

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[5] In Fig. 1(a), it is seen that while the agreement between the HPW calculations and experiment is excellent for the acoustic region of the spectrum, the observed optical peaks are not well described by the theory. Robbins and Page (Ref. 6) have shown that these peaks may be well accounted for by including non-zero electronic po-larizability derivatives on the defect's second as well as first nearest neighbors. Since the present paper is concerned with a comparison of the effects of using different lattice dynamical models for the host crystal, we will remain here within the context of the nearest-neighbor polarizability derivative model of HPW and Ref. 1.

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