# RAMAN SCATTERING AS A PROBE OF PURE-CRYSTAL PHONONS IN $\mathrm{Tl}^+$-DOPED POTASSIUM HALIDES*

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Raman scattering data are reported for $\mathrm{Tl}^+$ impurities in KCl, KBr, and KI. Strong lines of $E_g$ symmetry and weaker lines of $A_{1g}$, $E_g$, and $T_{2g}$ symmetry are observed. Theoretical calculations based on breathing-shell–model phonons, with no impurity-induced change in force constants, are seen to be in agreement with the data. It appears that $\mathrm{Tl}^+$ acts as an isotopic impurity and allows one to use the Raman effect as a direct probe of the pure-crystal phonons.

In this paper we report experimental data and theoretical calculations for Raman scattering in $\mathrm{Tl}^+$-doped KCl, KBr, and KI. Calculations of the Raman spectra, made with breathing-shell–model phonons, agree quite well with the data, without introducing any impurity-induced force-constant changes. The same parameters used for the Raman calculations were also used for a calculation of the $T_{1u}$ symmetry impurity modes, with results which are in close agreement with far-infrared, thermal conductivity, and specific-heat data for $\mathrm{Tl}^+$ in potassium halides. Since no force-constant changes are needed it appears that $\mathrm{Tl}^+$ in these crystals acts as an isotopic impurity, whose principal effect is to destroy the translational symmetry of the lattice. The Raman effect thus becomes a direct probe of the pure-crystal phonons.

Raman spectra were taken using a Spex double monochromator with photon-counting detection, and a Coherent Radiation Model No. 52 argon-ion laser, operating with 1.3 W in the 488.0-nm line. $\mathrm{Tl}^+$ concentrations in KCl and KI were $8.6\times10^{19}$ $\mathrm{cm}^{-3}$ and $6\times10^{18}$ $\mathrm{cm}^{-3}$, respectively. The $\mathrm{Tl}^+$ concentration in KBr was about $1\times10^{19}$ $\mathrm{cm}^{-3}$, but is uncertain since it was necessary to use the width of the $\mathrm{Tl}^+$ absorption band at 260 nm rather than its height to determine the concentration. The strengths of the Raman lines seen in KCl and KBr vary roughly as the concentration; only one concentration of $\mathrm{Tl}^+$ in KI was examined. The most important point is that first-order spectra are observed in doped crystals at these concentrations, which are all less than 0.5 mole%.

All three pure host materials show only a continous second-order Raman spectrum. Our spectra are in good agreement, both in frequency and symmetry assignment, with the KBr and KI spectra observed by Krauzman.[1] Introduction of $\mathrm{Tl}^+$ causes first-order lines to appear in the spectrum for all three hosts, as is illustrated by the Stokes spectrum for $\mathrm{KBr{:}Tl}^+$ in Fig. 1. The resolution is about 3 $\mathrm{cm}^{-1}$. This spectrum contains all symmetry modes superimposed. Impurity-induced lines are seen to appear at 71 and 82 $\mathrm{cm}^{-1}$, with additional scattering also seen near 125 $\mathrm{cm}^{-1}$. The temperature dependence of the

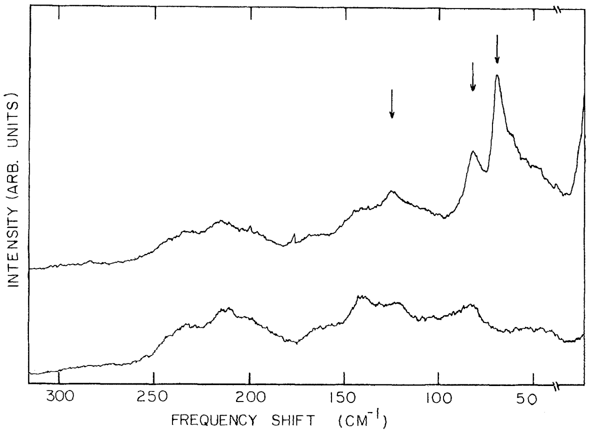

FIG. 1. Stokes spectra of pure and $\mathrm{Tl}^+$-doped KBr at room temperature. Upper curve, $\mathrm{KBr}+\mathrm{Tl}^+$; lower curve, pure KBr. Curves taken with same system gain.

ratio of Stokes to anti-Stokes peak heights for the impurity-induced lines is characteristic of a one-quantum process. None of the lines showed any measurable shift or narrowing with temperature down to 25°K. The relative strengths of the second-order spectra for the pure crystals, and of the first-order spectra for the $\mathrm{Tl}^+$-doped crystals, are in approximately the ratio $1:\frac{3}{4}:\frac{1}{3}$ (KI to KBr to KCl).

Symmetry properties of the impurity-induced lines and of the pure-crystal spectra can be obtained[1] by using various combinations of propagation direction of incident light, $\vec{k}$, polarization of incident light, $\vec{\epsilon}$, and the selected polarization of scattered light, $\vec{\epsilon}\,'$, relative to the crystal axes. In the usual 90° scattering geometry, $\vec{k} \parallel \langle 100\rangle$, $\vec{\epsilon} \parallel \langle 010\rangle$, and $\vec{\epsilon}\,' \parallel \langle 100\rangle$, one sees only Raman transitions of $T_{2g}$ character. (The point group for these materials is $O_h$.) Furthermore, $\vec{k} \parallel \langle 100\rangle$, $\vec{\epsilon} \parallel \langle 010\rangle$, and $\vec{\epsilon}\,' \parallel \langle 010\rangle$ allows $E_g + A_{1g}$, while $\vec{k} \parallel \langle 100\rangle$, $\vec{\epsilon} \parallel \langle 011\rangle$, and $\vec{\epsilon}\,' \parallel \langle 01\bar{1}\rangle$ permits only $E_g$.

We have examined all combinations for all crystals and find that the most prominent features of the impurity-induced spectra have $E_g$ symmetry. A typical room-temperature $E_g$ spectrum for KBr is shown in Fig. 2. The strongest impurity line is seen to be at 71 $\mathrm{cm}^{-1}$. The spectrum for KI is virtually identical to that for KBr, only scaled down in frequency; the strongest line in KI occurs at 51 $\mathrm{cm}^{-1}$. KCl has two strong $E_g$ lines at 113 and 135 $\mathrm{cm}^{-1}$. We shall refer to these four lines as the strong $E_g$ lines. Weaker $E_g$ lines can also be seen in Fig. 2, and in particular one notices a line at 109 $\mathrm{cm}^{-1}$ which could not be seen in Fig. 1; comparable lines are seen in KI and KCl. $T_{2g}$ lines with $\frac{1}{10}$ the intensity of the strong $E_g$ lines are observed in all crystals; a barely discernible $A_{1g}$ line is seen in KBr. A catalog of lines observed in all crystals is given in Table I, with an experimental uncertainty of about 2 $\mathrm{cm}^{-1}$ pertaining to all lines. A complete set of experimental and theoretical curves will be given in a more lengthy paper to be published later. One notices from Table I that lines of a given frequency often occur with more than one symmetry. This suggests that many of the lines listed in the table are characteristic of the pure materials themselves.

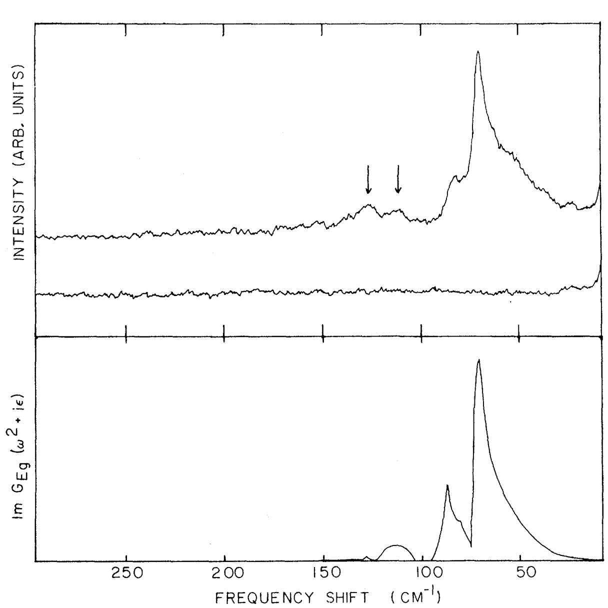

FIG. 2. Experimental and theoretical Stokes spectra for $E_g$ lines in KBr. Upper curve, KBr + $\mathrm{Tl}^+$ at room temperature; middle curve, pure KBr at same gain and temperature as top curve; lower curve, theoretical calculation described in the text.

Our first-order Raman scattering calculations are based on the off-resonance theory of Maradudin.[2] We assume that the electronic polarizability tensor is a linear function of the displacements of the six nearest neighbors of the defect. This gives a frequency-dependent part of the scattered Stokes intensity which is proportional to $N(\omega)\,\mathrm{Im}G_j(\omega^2+i\epsilon)$, where $N(\omega)$ is given by $[1-\exp(-\beta\hbar\omega)]^{-1}$. Here $G_j = (\Phi - \omega^2 M)_j{}^{-1}$ is the harmonic Green's function for the host-defect system, projected onto the $j$-type symmetry coordinates for the nearest neighbors. We have calculated the unperturbed $G_j$'s for $j = A_{1g}$, $E_g$, and $T_{2g}$ for a positive defect site in each of the three

Table I. Experimental and theoretical values of $\mathrm{Tl}^+$-induced impurity lines in various potassium halides (all entries in $\mathrm{cm}^{-1}$). Raman data in parentheses are only tentative since the lines are weak. Theory values in parentheses are only tentative since the calculated peaks are small.

| | | KCl | KBr | KI |
|---|---|---|---|---|
| $A_{1g}$ | Raman | -- | (82) | -- |
| | Theory | 129, 151 | 87, 114 | 63 |
| $E_g$ | Raman | 80, 113, 135 | 71, 82, 109, 123 | 51, 60, (113) |
| | Theory | 96, 116, 131 | 71, 87, 114, (128) | 55, 64, (105) |
| $T_{2g}$ | Raman | (110), 138 | (70), 82 | (50), 62 |
| | Theory | 75, 118, 150 | 60, 87, 121 | 41, 54, 63, 110 |
| $T_{1u}$ | Far IR | -- | -- | 67* |
| | Thermal Conductivity | 45** | 72** | 36** |
| | Specific Heat | 51*** | | |
| | Theory | 43 | 73 | 65 |

[a] From Sievers, Ref. 4.
[b] From Baumann and Pohl, Ref. 5.
[c] From Karlsson, Ref. 6.

host lattices, using phonon frequencies and polarization vectors obtained from the breathing shell model.[3]

A Brillouin-zone mesh of 64 000 $\vec{q}$ vectors was used, and the Green's functions were obtained as histograms with 100 bins of equal width $\Delta\omega^2$. The histograms were then plotted as functions of $\omega$, and the midpoints connected with straight-line segments, giving theoretical curves such as the one shown in Fig. 2 for $E_g$ modes in KBr. The overall agreement with the corresponding experimental curves is striking, particularly in view of the fact that no force-constant changes have been used. In addition to the peak positions, it is seen that the characteristic line shape of the strong $E_g$ line is well reproduced. Similar results pertain for the experimental and theoretical Raman spectra for KI; good agreement is also obtained for KCl, except for the lowest frequency $E_g$ line. Complete results are listed in Table I.

In view of the 2 $\text{cm}^{-1}$ uncertainty in the experimental spectra, and the uncertainties inherent in the histogram calculations of $G_j$, the agreement between the Raman and Theory entries in Table I is very good indeed. There are some discrepancies, most notably the 80- to 96-$\text{cm}^{-1}$ comparison for $E_g$ in KCl and the 60- to 70-$\text{cm}^{-1}$ comparison for $T_{2g}$ in KBr. Both could be due to experimental difficulties, especially in KBr where the (70)-$\text{cm}^{-1}$ line is admittedly weak.

We have also calculated the impurity-induced far-infrared absorption spectra for the odd-parity $T_{1u}$ resonances, using the $\text{Tl}^+$-$\text{K}^+$ mass difference and unchanged force constants. For polarizable defects the use of unperturbed force constants for the odd-parity $T_{1u}$ modes involves an additional assumption beyond those for the even-parity modes. In the language of the shell model the even-parity modes, for which the defect is at rest, are independent of changes in the defect's core-shell force constant and core and shell charges. Thus in our $T_{1u}$ calculations these quantities are assumed to be unperturbed.

Results of the $T_{1u}$ calculations are listed in Table I. Also listed is the frequency of the far-infrared resonance observed experimentally by Sievers[4] for KI:$\text{Tl}^+$, the $T_{1u}$ resonances deduced from thermal conductivity measurements by Baumann and Pohl,[5] and the resonance deduced from specific-heat measurements on KCl:$\text{Tl}^+$ by Karlsson.[6] The agreement between our calculations and these various experimental results is satisfactory, except for the KI:$\text{Tl}^+$ thermal conductivity resonance.

Pohl[7] has argued that $\text{Tl}^+$ is but one among many possible isotopic defects in potassium halides. We would suggest that some of his other candidates should be examined by the obviously sensitive Raman technique. It would also appear that $\text{Tl}^+$ in KCl and KBr should be examined in the far infrared.

Although the idea that isotopic impurities allow one to use Raman scattering as a probe of pure-crystal phonons is not new, its experimental realization is another matter. Hurrel et al.[8] have done a Raman experiment on KBr + 8% Cl. They found a line of $A_{1g}$ symmetry, but pointed out that their impurity concentration was high enough that it might be necessary to consider their system to be a disordered lattice. Their comment would be supported by the x-ray data of Vegard,[9] which demonstrates a lattice parameter change of 0.025 Å for 8% Cl in KBr.

In conclusion the present work provides the first unambiguous experimental example of a defect system for which the impurity allows one to use the Raman effect as a direct probe of the pure-crystal phonons.

We are indebted to Professor R. O. Pohl, who provided us with our most heavily doped KCl crystal, Professor A. J. Sievers, for interesting conversations, and Dr. A. V. Karlsson, for permitting us to quote his specific-heat data prior to publication.

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