

## LOCAL MODE FREQUENCIES DUE TO MONOVALENT IMPURITIES IN AgBr

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The local mode frequencies due to  $\text{Li}^+$  and  $\text{Na}^+$  impurities in AgBr were calculated using Green's function method. The perturbation model takes into account the change in mass at the impurity site and change in the nearest-neighbour central force constant between the impurity and the host ion. We have also obtained the effective force constant for the host lattice using the experimental local mode frequencies. To get a good fit with the experimental frequencies a 44% decrease in central forces is required in AgBr:  $\text{Li}^+$  whereas a 16% increase in central forces is seen in the case of AgBr:  $\text{Na}^+$ .

### 1. Introduction

Since the pioneering work of Schaeffer [1] on  $U$ -centre induced localized modes in alkali halides, a large amount of experimental as well as theoretical [2-5] work has been done on impurity induced infrared absorption. The main centre of attraction in these studies are alkali halides with the NaCl-structure. Recently, Hattori et al. [6, 7] have reported the experimental results on the impurity induced lattice absorption in silver halides. These authors have discussed their results of localized mode absorption taking a simple linear diatomic chain model with the mass defect given by Lucovsky et al. [8]. They have calculated the change in the force constant at the impurity site using the diatomic three dimensional model of Takeno [9]. From a theoretical point of view the most appropriate way to analyze the experimental results on impurity induced properties of solids is to use Green's function technique. This takes into account the entire phonon spectrum of the lattice and thus it is more realistic compared to other simple phenomenological models.

The purpose of the present paper is to calculate the local mode frequencies due to  $\text{Li}^+$  and  $\text{Na}^+$  impurities in AgBr using Green's function method. The central force point-ion model for the impurity host interaction is used in the calculations. This model is character-

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ized by change in mass at the impurity site and a change in the nearest neighbour central force constant between the impurity and the host ion. We have also obtained the effective force constant for the host lattice using the experimental local mode frequencies. The mass-defect calculation for the local mode frequencies are in better agreement with the experimental results than is that reported by Hattori et al. To fit the experimental frequencies a 44% decrease in central forces is required in AgBr: Li<sup>+</sup> whereas 16% increase in central forces is seen in the case of AgBr: Na<sup>+</sup>.

In order to calculate Green's function the necessary eigen frequencies and eigen vectors for AgBr were supplied by Bührer who calculated the lattice dynamics by using a modified shell model [10, 11].

## 2. Theory

### A. Perturbation model

The Green's functions matrix  $\mathbf{G}$  for the imperfect crystal is related to the Green's function matrix  $\mathbf{G}_0$  of the perfect crystal by the Dyson equation.

$$\mathbf{G} = (\mathbf{I} + \mathbf{G} \cdot \mathbf{P})^{-1} \mathbf{G}_0, \quad (1)$$

where  $\mathbf{P}$  is the perturbation matrix due to the presence of an impurity in the host lattice. Introducing  $\mathbf{T}$ -matrix, Eq. (1) can be written as

$$\mathbf{G} = \mathbf{G}_0 - \mathbf{G}_0 \mathbf{T} \mathbf{G}_0. \quad (2)$$

Here the  $\mathbf{T}$ -matrix is defined by

$$\mathbf{T} = \mathbf{P}(\mathbf{I} + \mathbf{G}_0 \mathbf{P})^{-1}. \quad (3)$$

For isolated impurities the non-zero elements of the  $\mathbf{P}$ -matrix lie in what is known as impurity space which comprises the impurity and its nearest neighbours. In the present case the impurity space consists of the space occupied by the impurity and its six nearest neighbours and thus the dimension of the  $\mathbf{P}$ -matrix is  $21 \times 21$ . By group theoretical arguments it is known that the modes corresponding to an irreducible representation transforming according to a polar vector can only interact with the incident light. In the present case the point group symmetry of the impurity site is  $O_h$ . The normal modes which transform according to the irreducible representation  $F_{1u}$  are infrared active. Using the necessary symmetry coordinates i.e. the symmetrized linear combinations of ionic displacements in the impurity space, the matrix  $\mathbf{P}$ , can be block diagonalized according to the different irreducible representation. The matrix elements of  $\mathbf{P}$  in the  $F_{1u}$  representation are:

$$\mathbf{P}_{F_{1u}} = \begin{pmatrix} -\varepsilon\omega^2 + 2\lambda + 4\lambda' & -(2x)^{1/2}\lambda & -2x^{1/2}\lambda' \\ -(2x)^{1/2}\lambda & x\lambda & 0 \\ -2x^{1/2}\lambda' & 0 & x\lambda' \end{pmatrix}, \quad (4)$$

where  $\varepsilon = \Delta M_{\pm}/M_{\pm}$  is the mass change parameter and  $x = M_{\pm}/M_{\mp}$  is the ratio of the masses of the ions of the two host sublattices.  $\lambda = \Delta r/M_{\pm}$  and  $\lambda' = \Delta r'/M_{\pm}$  are the changes in the central and non-central nearest neighbour effective force constants, respectively,

in units of squared frequency. The upper signs apply when the impurity occupies a positive ion site and the lower signs when it occupies a negative ion site.

If we denote the Green's function matrix for the unperturbed crystal in the impurity space by  $\mathbf{g}(z)$ , where  $z$  is the complex squared frequency,  $z = \omega^2 + 2i\omega\delta$ , in the limit as  $\delta \rightarrow 0_+$ , the matrix element of  $\mathbf{g}(z)$  for the  $F_{1u}$ -irreducible representation are seen to be

$$\mathbf{g}_{F_{1u}}(z) = \begin{pmatrix} g_1^\pm & \sqrt{2} g_2^\pm & 2g_3^\pm \\ \sqrt{2} g_2^\pm & g_1^\mp + g_7^\pm & 2\sqrt{2} g_4^\pm \\ 2g_3^\pm & 2\sqrt{2} g_4^\pm & g_1^\mp + 2g_5^\pm + g_8^\pm \end{pmatrix}, \quad (5)$$

where

$$\begin{aligned} g_1^\pm &= g_{xx}(0, 0, 0; 0, 0, 0), & g_2^\pm &= g_{xx}(0, 0, 0; 1, 0, 0), & g_3^\pm &= g_{yy}(0, 0, 0; 1, 0, 0), \\ g_4^\pm &= g_{xx}(1, 0, 0; 0, 1, 0), & g_5^\pm &= g_{zz}(1, 0, 0; 0, 1, 0), & g_6^\pm &= g_{xy}(1, 0, 0; 0, 1, 0), \\ g_7^\pm &= g_{xx}(1, 0, 0; -1, 0, 0), & g_8^\pm &= g_{yy}(1, 0, 0; -1, 0, 0). \end{aligned} \quad (6)$$

The explicit expression for the elements of the Green's function matrix  $\mathbf{g}(z)$  is given by

$$g_\zeta^\pm(z) = \frac{\Omega}{(2\pi)^3} \sum_{s=1}^6 \int_{\text{BZ}} \frac{j_\zeta(\vec{k}/s)}{\omega_{\vec{k},s}^2 - z} d\vec{k}, \quad (7)$$

where  $\Omega$  is the primitive unit cell volume of the lattice,  $s$  is the branch index,  $\vec{k}$  and  $\omega_{\vec{k},s}$  are the wave vectors and the frequency of the normal modes of the perfect lattice, respectively. The integration is carried over the first Brillouin zone (BZ). The  $j_\zeta^\pm$  are given by the following expressions:

$$\begin{aligned} j_1^\pm &= |e_x(\pm|\vec{k}s)|^2, & j_2^\pm &= e_x(\mp|\vec{k}s) e_x^*(\pm|\vec{k}s) \cos(\frac{1}{2} k_x a), \\ j_3^\pm &= e_x(\mp|\vec{k}s) e_x^*(\pm|\vec{k}s) \cos(\frac{1}{2} k_y a), & j_4^\pm &= |e_x(\mp|\vec{k}s)|^2 \cos(\frac{1}{2} k_x a) \cos(\frac{1}{2} k_y a), \\ j_5^\pm &= |e_x(\mp|\vec{k}s)|^2 \cos(\frac{1}{2} k_y a) \cos(\frac{1}{2} k_z a), & j_6^\pm &= e_x(\mp|\vec{k}s) e_y^*(\mp|\vec{k}s) \sin(\frac{1}{2} k_x a) \sin(\frac{1}{2} k_y a), \\ j_7^\pm &= |e_x(\mp|\vec{k}s)|^2 \cos(k_x a), & j_8^\pm &= |e_x(\mp|\vec{k}s)|^2 \cos(k_y a), \end{aligned} \quad (8)$$

where  $x, y, z = 1, 2, 3$  and  $x \neq y \neq z$ .

## B. Localized modes

The resonance denominator contained in the inverse matrix  $[\mathbf{I} + \mathbf{G}\mathbf{P}]^{-1}$  is of central importance in the study of defect modes. By separating its real and imaginary parts we have:

$$D(z) = \det |\mathbf{I} + \mathbf{g}(z)\mathbf{p}(\omega^2)| = \text{Re } D(z) + i \text{Im } D(z). \quad (9)$$

The frequencies of the localized, gap or resonance, modes are the solutions of the equation

$$\text{Re } D(z) = 0. \quad (10)$$

In the infrared active mode the resonance denominator is given by

$$D_{\text{Fiu}}(z) = 1 - \varepsilon\omega^2 g_1^\pm + \lambda[2g_1^\pm - 4\sqrt{x}g_2^\pm + x(g_1^\mp + g_7^\pm) - x\varepsilon\omega^2\{g_1^\pm(g_1^\mp + g_7^\pm) - 2g_2^{\pm 2}\}], \quad (11)$$

where we have put  $\lambda' = 0$ , i.e. only central forces are considered. Condition (10) is used to determine the changes in the central force constant. If only central forces are considered the lattice Green's functions for the perfect crystal are constrained by the site symmetry of the impurity and the relations between them can be obtained [12]. These relations for the NaCl-structure and in the present nearest neighbour defect model are seen to be

$$2\eta g_1^\pm - 2x^{1/2}\eta g_2^\pm = 1 + \omega^2 g_1^\pm, \quad 2\eta g_2^\pm - x^{1/2}\eta(g_1^\mp + g_7^\pm) = \omega^2 g_2^\pm. \quad (12)$$

Here,  $\eta = r/M_\pm$  is the nearest neighbour effective force constant for the perfect lattice. Using these relations the resonance denominator (11) simplifies to

$$D_{\text{Fiu}}(z) = (1 + \beta)(1 - \varepsilon\omega^2 g_1^\pm) + \beta(1 + \varepsilon)(\omega^2/2\eta)(1 + \omega^2 g_1^\pm), \quad (13)$$

where  $\beta = \lambda/\eta$  is the relative change in central force constant. It is noted that only same-site Green's function  $g_1^\pm$  is required in equation (13). Using the two forms of the resonance denominator  $D_{\text{Fiu}}(z)$  (Eqs. (11), (13)), the nearest-neighbour effective force constant for pure crystal is easily evaluated.

### 3. Numerical computations and results

#### A. Green's functions

In order to calculate the complex Green's functions defined by equations (7) and (8) a staggered bin averaging procedure is followed. The quantities given in Eq. (8) were calculated first and sorted by dividing the frequency interval into sixty equal bins. The resulting histograms were used to calculate the imaginary and real parts of the Green's functions separately. To carry out the numerical integration in the real part of the Green's functions, the method suggested by Maradudin was followed. In these summations a grid of 4,000 uniformly distributed  $\vec{k}$ -points inside the Brillouin zone was employed.

In carrying out the integration, the frequency increment used is of vital importance, especially when a finite number of distinct  $\vec{k}$ -points in the Brillouin zone have been used. A value of the frequency increment that is too small will cause spurious fluctuations in Green's functions, while with a value too large the frequency dependent nature of Green's function will be lost. For the present choice of 4,000 points in the Brillouin zone, a value of 0.4 for the frequency increment in units of bins was found to be appropriate and was used in the calculations.

The required normal mode frequencies and eigen vectors of AgBr were kindly supplied to us by Bührer [11]. As a representative case the real and imaginary parts of the Green's function  $g_1^+$  are shown in Figure 1.

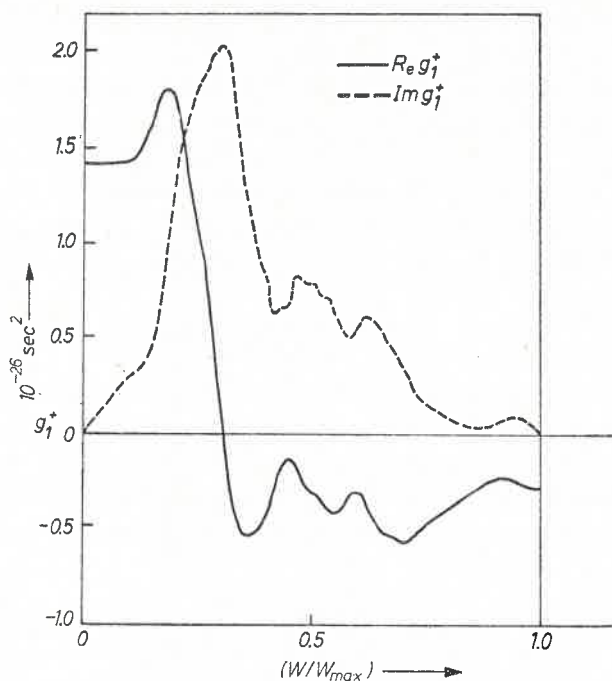


Fig. 1. Calculated real and imaginary parts of the Green's function  $g_1^*$  for AgBr

### B. Local modes

We now consider Eq. (10) to determine the impurity modes in AgBr. For  $\lambda = 0$  this equation reduces to the isotopic defect approximation

$$1 - \varepsilon\omega^2 g_1 = 0. \quad (14)$$

TABLE I

Localized mode frequency ( $\text{cm}^{-1}$ ) and the force constant change due to  ${}^6\text{Li}^+$ ,  ${}^7\text{Li}^+$  and  $\text{Na}^+$  in AgBr

Systems	$\omega_L^a$ (exp)	$\omega_L$ (cal)	$\omega_{\text{theor}}^a$	$\lambda$
Ag Br: ${}^6\text{Li}^+$	205.9	262.10	311.8	$-0.31 \times 10^{26} \text{ sec}^{-2}$
Ag Br: ${}^7\text{Li}^+$	191.8	246.45	289.6	$-0.32 \times 10^{26} \text{ sec}^{-2}$
Ag Br: $\text{Na}^+$	166.7	157.09	168.8	$0.12 \times 10^{26} \text{ sec}^{-2}$

<sup>a</sup> Reference [7].

This equation was used to calculate the local mode frequencies due to  ${}^6\text{Li}^+$ ,  ${}^7\text{Li}^+$  and  $\text{Na}^+$  and these are shown in Table I along with the experimental values and values calculated by Hattori et al. [7]. To fit the experimental frequencies the required value of the central force constant changes determined by equations (10) and (11) are included in Table I.

From Table I it can be seen that the calculated localized mode frequencies in a mass defect approximation in lithium doped crystals are in better agreement with the experimental results than the theoretical results obtained by Hattori et al. [7] in a linear diatomic chain model. In the case of AgBr: Na<sup>+</sup> our calculated value for the localized mode frequency is less than the experimental results which is not surprising in view of the obtained increase in the force constant as a result of fitting the experimental frequency. This result is in accord with the fact that the effect of force constant hardening is to push the localized mode frequency away from the band-edge, whereas the opposite occurs with force constant softening [14-16].

We also see from Table I that the experimental local mode frequencies,  $\omega_{L \text{ Exp}}(^6\text{Li}^+)$  and  $\omega_{L \text{ Exp}}(^7\text{Li}^+)$ , are explained by the value of  $\lambda = -0.31 \times 10^{26} \text{ sec}^{-2}$  and  $\lambda = -0.32 \times 10^{26} \text{ sec}^{-2}$ , respectively. Because  $^6\text{Li}^+$  and  $^7\text{Li}^+$  are isotopes of the same ion we expect the experimental values of  $\omega_L(^6\text{Li}^+)$  and  $\omega_L(^7\text{Li}^+)$  to be reproduced by the same value of  $\lambda$ , and this is found almost to be the case in the present work. Thus, the lithium impurity can be described by an Einstein oscillator and the frequency ratio of two localized modes due to Li isotopes is equal to the square root of the inverse ratio of these impurity masses, that is,

$$\frac{\omega_L(^6\text{Li})}{\omega_L(^7\text{Li})} = \left( \frac{M_{^7\text{Li}}}{M_{^6\text{Li}}} \right)^{1/2} = 1.080, \quad (15)$$

which is fairly close to the ratio 1.074 of experimentally determined localized frequencies due to  $^6\text{Li}^+$  and  $^7\text{Li}^+$ .

Now using the calculated values of the force constant change and the experimentally localized mode frequencies, the effective force constant for the perfect crystal is easily calculated using equations (11) and (13). The calculated values of the effective force constant ( $2\eta$ ) is found to be  $1.42 \times 10^{26} \text{ sec}^{-2}$ ,  $1.44 \times 10^{26} \text{ sec}^{-2}$  and  $1.50 \times 10^{26} \text{ sec}^{-2}$  corresponding to the systems AgBr:  $^6\text{Li}^+$ , AgBr:  $^7\text{Li}^+$  and AgBr: Na<sup>+</sup>, respectively. These values may be compared with

$$\frac{e^2}{2v} \frac{A}{M_+} = 1.59 \times 10^{26} \text{ sec}^{-2},$$

where  $A$  is the nearest neighbour central force constant used in the shell model calculation of lattice dynamics by Bührer [6, 7].

#### 4. Conclusion

By employing a simple perturbation model for the impurity that includes the change in mass at the impurity site along with the changes in the nearest neighbour central force constants we have studied the dynamics of imperfect AgBr crystals based on a Green's function technique. The changes in the nearest neighbour central force constant due to  $^6\text{Li}^+$ ,  $^7\text{Li}^+$  and Na<sup>+</sup> ions was calculated by fitting the local mode frequencies with the experimental data. The change in the central force constant and the experimental values

of the localized mode frequency were used to calculate the nearest neighbour effective force constant in a perfect crystal.

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