Infrared Absorption due to Substitutional Impurity in Cubic Crystals

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The explicit expressions have been obtained for the absorption line-shape function due to one-phonon processes in some models of cubic crystals with impurities. All of them show pronounced resonance peaks in the low-frequency region for heavy impurities. Similar resonances also occur for light impurities when the force constants are reduced. An estimate is made of the change in force constant in the case of Li^6 and Li^7 in KBr, based on the experimental data of Sievers and Takeno.

INTRODUCTION

THERE has been considerable interest in recent years in the optical absorption of crystals with impurities in the far infrared, because of the direct link between the absorption line shape and the structure of the phonon spectrum in the impure crystal. Crystals with charged impurities and ionic crystals with substitutional impurities have been studied both experimentally[1,2] and theoretically.[3–5] The theoretical work in this area has mostly been with the so-called mass defect approximation in which the difference between the mass of the impurity and that of the normal atom it replaces is the only parameter characterizing the perturbation due to the impurity. A more realistic model of the impurity would naturally have to take into account the change in the force constants associated with the impurity besides the change in mass. There is an intimate relationship between the solution of phonon scattering from such an impurity[6,7] and the solution of the problem of infrared absorption. The object of this paper is to exploit the relationship and obtain exact expressions for the absorption line shape in certain solvable models of impure crystals.

THEORY

The Hamiltonian of a monatomic crystal in the harmonic approximation is given by

$$H=\sum_{\mathbf{l},\alpha}\frac{p_{\mathbf{l},\alpha}^2}{2m_{\mathbf{l}}}+\tfrac{1}{2}\sum_{\mathbf{l},\mathbf{n};\alpha,\beta}\Phi_{\alpha\beta}{}^{\mathbf{ln}}u_{\mathbf{l},\alpha}u_{\mathbf{n},\beta}\,, \tag{1}$$

where Latin letters refer to the lattice sites and Greek letters refer to the Cartesian components of the displacements of the atoms. $m_{\mathbf{l}}$ is the mass of the lth atom and $\Phi_{\alpha\beta}{}^{\mathbf{ln}}$ are the elements of the force constant matrix.

If the charge of the lth atom is $e_{\mathbf{l}}$, the electric field of the incident radiation generates a current density of the form[8]

$$J_\alpha(t)=\mathrm{Re}\sum_\beta\sigma_{\alpha\beta}(\omega)E_\beta e^{i\omega t+\epsilon t}\,, \tag{2}$$

where the element of the electrical conductivity tensor $\sigma_{\alpha\beta}(\omega)$ is given by

$$\sigma_{\alpha\beta}(\omega)=-\frac{i}{\omega}\sum_{\mathbf{l}}\frac{e_{\mathbf{l}}{}^2}{m_{\mathbf{l}}}\delta_{\alpha\beta}-i\times\int_{-\infty}^{\infty}\theta(-\tau)\langle\langle J_\alpha(0),J_\beta(\tau)\rangle\rangle\frac{e^{i\omega\tau+\epsilon\tau}}{i\omega+\epsilon}d\tau\,, \tag{3}$$

and the current operator $J_\alpha(t)$ is given by

$$J_\alpha(t)=\sum_{\mathbf{l}}e_{\mathbf{l}}\dot{u}_{\mathbf{l},\alpha}(t)\,. \tag{4}$$

The double bracket $\langle\langle\ \ \rangle\rangle$ stands for thermal averaging of the commutator and ω is the frequency of the radiation.

In terms of the retarded Green's function defined by

$$F_{\alpha\beta}(\mathbf{l},\mathbf{l}';t)=-i(m_{\mathbf{l}}m_{\mathbf{l}'})^{1/2}\langle\langle\dot{u}_{\mathbf{l},\alpha}(0),\dot{u}_{\mathbf{l}',\beta}(t)\rangle\rangle\theta(-t)\,, \tag{5}$$

and its Fourier transform

$$F_{\alpha\beta}(\mathbf{l},\mathbf{l}';\omega)=\int_{-\infty}^{\infty}e^{i\omega t}F_{\alpha\beta}(\mathbf{l},\mathbf{l}';t)dt\,, \tag{6}$$

the conductivity tensor becomes

$$\sigma_{\alpha\beta}(\omega)=-\frac{i}{\omega}\sum_{\mathbf{l}}\frac{e_{\mathbf{l}}{}^2}{m_{\mathbf{l}}}\delta_{\alpha\beta}+\sum_{\mathbf{l},\mathbf{l}'}\frac{e_{\mathbf{l}}e_{\mathbf{l}'}}{(m_{\mathbf{l}}m_{\mathbf{l}'})^{1/2}}\frac{F_{\alpha\beta}(\mathbf{l},\mathbf{l}';\omega)}{i\omega+\epsilon}\,. \tag{7}$$

The equation of motion of $F_{\alpha\beta}(\mathbf{l},\mathbf{l}';t)$ is given by

$$\frac{d^2}{dt^2}F_{\alpha\beta}(\mathbf{l},\mathbf{l}';t)=-\delta(-t)\frac{\Phi_{\alpha\beta}{}^{\mathbf{ll}'}}{(m_{\mathbf{l}}m_{\mathbf{l}'})^{1/2}}-\sum_{\mathbf{j},\gamma}F_{\alpha\gamma}(\mathbf{l},\mathbf{j};t)\frac{\Phi_{\gamma\beta}{}^{\mathbf{jl}'}}{(m_{\mathbf{j}}m_{\mathbf{l}'})^{1/2}}\,, \tag{8}$$

[1] A. J. Sievers, Phys. Rev. Letters **13**, 310 (1964); A. J. Sievers and S. Takeno, Phys. Rev. **140**, A1030 (1965).
[2] J. F. Angress, A. R. Goodwin, and S. D. Smith, Proc. Roy. Soc. (London) **A287**, 64 (1965).
[3] R. J. Elliott and P. G. Dawber, Proc. Phys. Soc. (London) **81**, 453 (1963).
[4] R. J. Elliott, J. Phys. Chem. Solids Suppl. **1**, 459 (1965).
[5] S. Takeno, Progr. Theoret. Phys. (Kyoto) **33**, 363 (1965).
[6] J. Callaway, J. Math. Phys. **5**, 783 (1964).
[7] M. Yussouff and J. Mahanty, Proc. Phys. Soc. (London) **85**, 1223 (1965).
[8] D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [English transl.: Soviet Phys.—Usp. **3**, 320 (1960)].

or, in a matrix form,

$$\frac{d^2}{dt^2}\mathbf{F}(t)=-\delta(-t)\mathbf{D}-\mathbf{F}\mathbf{D}, \tag{9}$$

where

$$\mathbf{D}=\mathbf{M}^{-1/2}\mathbf{\Phi}\mathbf{M}^{-1/2} \tag{10}$$

and

$$\mathbf{M}=\text{the mass matrix.} \tag{11}$$

Taking the Fourier transform of Eq. (9), we obtain

$$\begin{aligned}\mathbf{F}(\omega)&=-\mathbf{I}+\mathbf{I}\omega^2(\mathbf{I}\omega^2-\mathbf{D})^{-1}\\&=-\mathbf{I}+\omega^2\mathbf{M}^{1/2}\mathbf{G}\mathbf{M}^{1/2},\end{aligned} \tag{12}$$

where

$$\mathbf{G}=(\mathbf{M}\omega^2-\mathbf{\Phi})^{-1}. \tag{13}$$

$\mathbf{G}$ is the Green's-function matrix whose elements have been discussed by Lifshitz,[9] and Montroll and Potts.[10]

The power absorption per unit volume as a function of the frequency is given by

$$\begin{aligned}B(\omega)&=\langle\sum_\alpha E_\alpha(t)J_\alpha(t)\rangle_t\\&=\langle\sum_\alpha E_\alpha\cos\omega t\times\mathrm{Re}\sum_\beta\sigma_{\alpha\beta}(\omega)E_\beta e^{i\omega t+\epsilon t}\rangle_t\\&=\sum_{\mathbf{l},\mathbf{l}';\alpha,\beta}\tfrac{1}{2}e_{\mathbf{l}}e_{\mathbf{l}'}E_\alpha E_\beta\omega\,\mathrm{Im}G_{\alpha\beta}(\mathbf{l},\mathbf{l}';\omega).\end{aligned} \tag{14}$$

In this, $\langle\ \rangle_t$ means the time average, and use has been made of Eqs. (7) and (12).

This is an exact expression for the line-shape function in a harmonic lattice when the absorption is due to a one-phonon process. We shall use it in some specific cases in which the explicit form of the Green's function of the impure crystal can be evaluated easily.

Charged Impurity in Monatomic Cubic Lattices

We shall consider here the absorption due to a charged impurity in a monatomic cubic lattice with nearest-neighbor central and noncentral forces, of the type considered by Montroll and Potts.[10] We shall assume that the nearest-neighbor central and noncentral force constants are the same in the normal crystal and that the mass and force constants associated with the impurity atom are different from those characterizing the normal atom. Then,

$$\begin{aligned}&E_\beta=E_0\delta_{\alpha\beta}, \quad e_{\mathbf{l}}=e\delta_{\mathbf{l},\mathbf{0}};\\&e_{\mathbf{l}'}=e\delta_{\mathbf{l}',\mathbf{0}}, \quad m_{\mathbf{l}}=M(1-\delta_{\mathbf{l},\mathbf{0}})+(M+\Delta M)\delta_{\mathbf{l},\mathbf{0}};\end{aligned} \tag{15}$$

and

$$B(\omega)=\tfrac{1}{2}e^2E_0^2\omega\,\mathrm{Im}G(\mathbf{0},\mathbf{0};\omega) \tag{16}$$

where e is the charge of the impurity, and $G(\mathbf{0},\mathbf{0};\omega)$ is the $(\mathbf{0},\mathbf{0})$th element of the perturbed Green's function.

[9] I. M. Lifshitz, Nuovo Cimento Suppl. **3**, 716 (1956).
[10] E. W. Montroll and R. B. Potts, Phys. Rev. **100**, 525 (1955).

Substitutional Impurity in a Diatomic Simple Cubic Lattice

This model is similar to that of Mitani and Takeno.[11] The lattice consists of atoms having two types of masses M_1 and M_2 with charges e and $-e$ situated alternately at even and odd sites, respectively, with interactions similar to those in the previous case. The impurity whose mass and nearest-neighbor force constants are $M_1+\Delta M$, and $\gamma+\Delta\gamma$, respectively, is situated at the origin. Thus,

$$\begin{aligned}&e_{\mathbf{l}}=(-1)^{l_1+l_2+l_3}e,\\&E_\beta=E_0\delta_{\alpha\beta},\\&m_{\mathbf{l}}=M_1\delta_{l_1+l_2+l_3,\mathrm{even}}+M_2\delta_{l_1+l_2+l_3,\mathrm{odd}},\end{aligned} \tag{17}$$

and

$$B(\omega)=\tfrac{1}{2}e^2\omega E_0^2\,\mathrm{Im}\sum_{\mathbf{l}\mathbf{l}'}(-1)^{\Sigma(l+l')_i}(\mathbf{M}\omega^2-\mathbf{\Phi})_{\mathbf{l}\mathbf{l}'}{}^{-1}. \tag{18}$$

But the diatomic cubic lattice can be treated as a monatomic cubic lattice by the M^* transformation,[12]

$$(\mathbf{M}^*\omega^2-\mathbf{\Phi})=\mathbf{S}'(\mathbf{M}\omega^2-\mathbf{\Phi})\mathbf{S}^{-1}, \tag{19}$$

where $\mathbf{S}'$ and $\mathbf{S}^{-1}$ are diagonal matrices having elements

$$\begin{aligned}S_{\mathbf{l},\mathbf{l}'}=\delta_{\mathbf{l}\mathbf{l}'}[&(M_1\omega^2-6\gamma)^{1/2}\delta_{\Sigma l_i,\mathrm{even}}\\&+(M_2\omega^2-6\gamma)^{1/2}\delta_{\Sigma l_i,\mathrm{odd}}],\end{aligned} \tag{20}$$

$$\begin{aligned}S'_{\mathbf{l},\mathbf{l}'}=\delta_{\mathbf{l}\mathbf{l}'}[&(M_2\omega^2-6\gamma)^{1/2}\delta_{\Sigma l_i,\mathrm{even}}\\&+(M_1\omega^2-6\gamma)^{1/2}\delta_{\Sigma l_i,\mathrm{odd}}],\end{aligned} \tag{21}$$

and

$$M^*\omega^2=[(M_1\omega^2-6\gamma)(M_2\omega^2-6\gamma)]^{1/2}+6\gamma. \tag{22}$$

Hence the Green's-function matrix occurring in Eq. (18) can be written as

$$(\mathbf{M}\omega^2-\mathbf{\Phi})^{-1}=\mathbf{S}^{-1}(\mathbf{M}^*\omega^2-\mathbf{\Phi})^{-1}\mathbf{S}', \tag{23}$$

and $B(\omega)$ becomes

$$\begin{aligned}B(\omega)=\tfrac{1}{2}e^2E_0^2\omega\,\mathrm{Im}\sum_{\mathbf{l}\mathbf{l}'}&\left[\frac{\delta_{\Sigma l_i,\mathrm{even}}}{(M_1\omega^2-6\gamma)^{1/2}}-\frac{\delta_{\Sigma l_i,\mathrm{odd}}}{(M_2\omega^2-6\gamma)^{1/2}}\right]\\&\times(\mathbf{M}^2\omega^2-\mathbf{\Phi})^{-1}{}_{\mathbf{l}\mathbf{l}'}[M_2\omega^2-6\gamma)^{1/2}\delta_{\Sigma l_{i'},\mathrm{even}}\\&-(M_1\omega^2-6\gamma)^{1/2}\delta_{\Sigma l_{i'},\mathrm{odd}}].\end{aligned} \tag{24}$$

Evaluation of the Perturbed Green's Functions

The perturbed and unperturbed Green's functions are related by the equation

$$\mathbf{G}=\mathbf{G}^0-\mathbf{G}^0\mathbf{P}\mathbf{G}=(\mathbf{I}+\mathbf{G}^0\mathbf{P})^{-1}\mathbf{G}^0, \tag{25}$$

where $\mathbf{G}^0$ is the unperturbed Green's function matrix, and $\mathbf{P}$ is the perturbation matrix.

[11] Y. Mitani and S. Takeno, Progr. Theoret. Phys. (Kyoto) **33**, 779 (1965).
[12] E. W. Montroll and R. B. Potts, Phys. Rev. **102**, 72 (1956).

The perturbation matrix has a simple form, as its effect is restricted to the impurity site and its nearest neighbors. In scalar lattice models, i.e., models in which the phonons are unpolarized, the nonvanishing elements of the perturbation matrix constitute a submatrix whose dimension is 7 for simple cubic, 9 for bcc, and 13 for fcc lattices.

We can write the perturbation matrix in the following partitioned form:

$$\mathbf{P}=\begin{bmatrix}\mathbf{p} & 0 & 0 & \cdots\\ 0 & 0 & 0 & \cdots\\ 0 & 0 & 0 & \cdots\\ \cdots & \cdots & \cdots & \cdots\\ \cdots & \cdots & \cdots & \cdots\end{bmatrix}. \tag{26}$$

Similarly the Green's-function matrix can be written as

$$\mathbf{G}^0=\begin{bmatrix}\mathbf{g} & \mathbf{g}_{12} & \mathbf{g}_{13} & \cdots\\ \mathbf{g}_{21} & \mathbf{g}_{22} & \mathbf{g}_{23} & \cdots\\ \cdots & \cdots & \cdots & \cdots\end{bmatrix}, \tag{27}$$

where each of the submatrices of $\mathbf{G}^0$ has the same dimension as that of $\mathbf{p}$. Making use of these two equations, Eq. (25) can be written in the form

$$\mathbf{G}=\mathbf{G}^0+\mathbf{A}\mathbf{G}^0, \tag{28}$$

where

$$\mathbf{A}=\begin{bmatrix}-\mathbf{g}\mathbf{p}(\mathbf{I}+\mathbf{g}\mathbf{p})^{-1} & 0 & 0 & \cdots\\ -\mathbf{g}_{21}\mathbf{p}(\mathbf{I}+\mathbf{g}\mathbf{p})^{-1} & 0 & 0 & \cdots\\ -\mathbf{g}_{31}\mathbf{p}(\mathbf{I}+\mathbf{g}\mathbf{p})^{-1} & 0 & 0 & \cdots\\ \cdots & \cdots & \cdots & \cdots\end{bmatrix}. \tag{29}$$

In the case of the charged impurity we need only the $(\mathbf{0},\mathbf{0})$th element of $\mathbf{G}$, i.e.,

$$\mathbf{G}(\mathbf{0},\mathbf{0};\omega)=[\{\mathbf{I}-\mathbf{g}\mathbf{p}(\mathbf{I}+\mathbf{g}\mathbf{p})^{-1}\}\mathbf{g}]_{0,0}. \tag{30}$$

The element of the matrix on the right-hand side of Eq. (30) can be obtained by group theoretic techniques.[7] It has been shown[13] that the $(\mathbf{0},\mathbf{0})$th element is contained in the block corresponding to the totally symmetric irreducible representation, when the matrix is block diagonalized into the irreducible representations of the point group of the lattice. The form of $\mathbf{G}(\mathbf{0},\mathbf{0};\omega)$ for the cubic lattices in the scalar model is

$$G_S(\mathbf{0},\mathbf{0};\omega)=\frac{1}{F_{SS}}\left[\left(1+\frac{E_S}{3}\frac{\Delta\gamma}{\gamma}\right)g_{0S}+\frac{1}{6\gamma}\frac{\Delta\gamma}{\gamma}\right], \tag{31}$$

$$G_B(\mathbf{0},\mathbf{0};\omega)=\frac{1}{F_{SB}}\left[\left(1+E_B\frac{\Delta\gamma}{\gamma}\right)g_{0B}+\frac{1}{8\gamma}\frac{\Delta\gamma}{\gamma}\right], \tag{32}$$

$$G_F(\mathbf{0},\mathbf{0};\omega)=\frac{1}{F_{SF}}\left[\left(1+\frac{E_F}{3}\frac{\Delta\gamma}{\gamma}\right)g_{0F}+\frac{1}{12\gamma}\frac{\Delta\gamma}{\gamma}\right]. \tag{33}$$

Here and in what follows the subscripts S, B, and F refer to simple cubic, bcc, and fcc lattices, respectively F_S is the S-type (totally symmetric) factor in the determinant $|\mathbf{I}+\mathbf{g}\mathbf{p}|$.

The explicit forms of F_S are

$$F_{SS}=\left(1+\frac{\Delta\gamma}{\gamma}\right)\left[1+\tfrac{2}{3}\Delta\gamma(3-E_S)\left(E_S g_{0S}+\frac{1}{2\gamma}\right)\right]+2\gamma\left(\frac{\Delta M}{M}-\frac{\Delta\gamma}{\gamma}\right)(3-E_S)\times\left[\left(1+\frac{E_S}{3}\frac{\Delta\gamma}{\gamma}\right)g_{0S}+\frac{1}{6\gamma}\frac{\Delta\gamma}{\gamma}\right], \tag{34}$$

$$F_{SB}=\left(1+\frac{\Delta\gamma}{\gamma}\right)\left[1+8\Delta\gamma(1-E_B)\left(E_B g_{0B}+\frac{1}{8\gamma}\right)\right]+8\gamma\left(\frac{\Delta M}{M}-\frac{\Delta\gamma}{\gamma}\right)(1-E_B)\times\left[\left(1+E_B\frac{\Delta\gamma}{\gamma}\right)g_{0B}+\frac{1}{8\gamma}\frac{\Delta\gamma}{\gamma}\right], \tag{35}$$

$$F_{SF}=\left(1+\frac{\Delta\gamma}{\gamma}\right)\left[1+\tfrac{4}{3}\Delta\gamma(3-E_F)\left(E_F g_{0F}+\frac{1}{4\gamma}\right)\right]+4\gamma\left(\frac{\Delta M}{M}-\frac{\Delta\gamma}{\gamma}\right)(3-E_F)\times\left[\left(1+\frac{E_F}{3}\frac{\Delta\gamma}{\gamma}\right)g_{0F}+\frac{1}{12\gamma}\frac{\Delta\gamma}{\gamma}\right]. \tag{36}$$

Here,

$$E_S=3-\frac{M}{2\gamma}\omega^2, \tag{37}$$

$$E_B=1-\frac{M}{8\gamma}\omega^2, \tag{38}$$

$$E_F=3-\frac{M}{4\gamma}\omega^2, \tag{39}$$

and

$$g_0=\frac{\Omega}{M(2\pi)^3}\int\int\int\frac{d^3k}{\omega^2-\omega^2(\mathbf{k})-i\epsilon}. \tag{40}$$

Ω has the value 1 for simple cubic, $\frac{1}{2}$ for bcc, and $\frac{1}{4}$ for fcc lattices, and $\omega(\mathbf{k})$ is the corresponding dispersion relation. Substituting the imaginary parts of Eqs. (31) to (33) in Eq. (16), one obtains the line-shape function due to a charged impurity in the three cubic lattices.

For the diatomic cubic lattice, we have to sum over $\mathbf{l}$ and $\mathbf{l}'$ in Eq. (24). Here the perturbation matrix is similar to that in the simple cubic lattice, but differs by a multiplicative factor β for $\sum_i l_i$ even and $\sum_i l_i'$

[13] K. Patnaik and J. Mahanty, Technical Report No. 5, Department of Physics, Indian Institute of Technology, Kanpur, India, 1965 (unpublished).

even, and β^{-1} if $\sum_i l_i$ odd and $\sum_i l_i'$ odd. β is given by

$$\beta=\left(\frac{M_2\omega^2-6\gamma}{M_1\omega^2-6\gamma}\right)^{1/2}. \tag{41}$$

Substitution of the first term of Eq. (28) in Eq. (24) gives the power absorption in the perfect crystal,

$$B_{\text{perfect}}(\omega)=\tfrac{1}{4}N\omega e^2E_0^2\left(\frac{M_1+M_2}{M_1M_2}\right)\operatorname{Im}\frac{1}{\omega^2-\omega_m^2-i\epsilon}$$

$$=\tfrac{1}{4}N\pi\omega e^2E_0^2\left(\frac{M_1+M_2}{M_1M_2}\right)\delta(\omega^2-\omega_m^2), \tag{42}$$

where the maximum frequency of the crystal ω_m is given by

$$\omega_m^2=\frac{6\gamma(M_1+M_2)}{M_1M_2}.$$

This absorption line corresponds to the wave vector $\mathbf{k}=0$, and is well known.

The second term of Eq. (28) is the contribution of the impurity to power absorption. When $\mathbf{AG}^0$ is substituted in Eq. (24), the summation over $\mathbf{l}'$ can be carried out easily, because it occurs in the exponential in the integrand of the integrals for the elements of $\mathbf{G}^0$. The structure of the $\mathbf{A}$ matrix is such that it has non-vanishing elements only up to the column whose index corresponds to the last lattice site affected by the impurity. This enables us to write Eq. (24) as

$$B_{\text{Impurity}}(\omega)=\tfrac{1}{2}\omega e^2E_0^2\operatorname{Im}\frac{1}{4a}\Bigg[\frac{\{(M_1+M_2)\omega^2-12\gamma+2a\}}{a-6\gamma}\sum_{\mathbf{l},\Delta'}e^{i(\mathbf{l}+\Delta')\pi}A_{\mathbf{l},\Delta'}+\frac{\{(M_1+M_2)\omega^2-12\gamma-2a\}}{a+6\gamma}$$

$$\times\sum_{\mathbf{l},\Delta'}A_{\mathbf{l},\Delta'}+\frac{(M_2-M_1)\omega^2}{a+6\gamma}\sum_{\mathbf{l},\Delta'}e^{i\mathbf{l}\pi}A_{\mathbf{l},\Delta'}+\frac{(M_2-M_1)\omega^2}{a-6\gamma}\sum_{\mathbf{l},\Delta'}e^{i\Delta'\pi}A_{\mathbf{l},\Delta'}\Bigg], \tag{43}$$

where $\mathbf{\Delta}'$ runs over all the affected lattice sites. Here a is given by

$$a=[(M_1\omega^2-6\gamma)(M_2\omega^2-6\gamma)]^{1/2}. \tag{44}$$

The summation over $\mathbf{l}$ can be performed by making use of the partitioned form of $\mathbf{A}$, and then we obtain

$$B_{\text{Impurity}}(\omega)=-\tfrac{1}{2}\omega e^2E_0^2\operatorname{Im}\frac{1}{4a}\Bigg[\frac{\{(M_1+M_2)\omega^2-12\gamma+2a\}}{(a-6\gamma)^2}\sum_{\Delta,\Delta'}[\mathbf{p}^*(\mathbf{l}+\mathbf{g}^*\mathbf{p}^*)^{-1}]_{\Delta,\Delta'}e^{i\pi(\Delta+\Delta')}$$

$$+\frac{\{(M_1+M_2)\omega^2-12\gamma-2a\}}{(a+6\gamma)^2}\sum_{\Delta,\Delta'}[\mathbf{p}^*(\mathbf{l}+\mathbf{g}^*\mathbf{p}^*)^{-1}]_{\Delta,\Delta'}+\frac{(M_2-M_1)\omega^2}{a^2-36\gamma^2}\sum_{\Delta,\Delta'}(e^{i\pi\Delta}+e^{i\pi\Delta'})[\mathbf{p}^*(\mathbf{l}+\mathbf{g}^*\mathbf{p}^*)^{-1}]_{\Delta,\Delta'}\Bigg]. \tag{45}$$

Here the asterisk refers to the lattice obtained by the M^* transformation.

In order to sum over $\mathbf{\Delta}$ and $\mathbf{\Delta}'$ in the above expression we adopt the following procedure: Since the submatrices $\mathbf{p}^*$ and $\mathbf{g}^*$ have the symmetry of the point group of the crystal, the matrix $\mathbf{p}^*(\mathbf{l}+\mathbf{g}^*\mathbf{p}^*)^{-1}$ can be block diagonalized by a unitary matrix $\mathbf{V}$ into diagonal submatrices belonging to the different irreducible representations of the point group that occur in the reducible representation generated by the affected lattice sites. Of these, only the totally symmetric or S part contributes to the above sum and becomes infrared active. The sums involving the other irreducible representation vanish. Hence,

$$B_{\text{Impurity}}(\omega)=-\tfrac{1}{2}\omega e^2E_0^2\operatorname{Im}(Q/F_S^*), \tag{46}$$

where

$$Q=\frac{6\gamma}{M_1M_2(\omega^2-\omega_m^2)^2}\Bigg[\left(\frac{\Delta M}{M_1}\right)\frac{\omega^2}{\omega_0^2}\left\{\sigma\left(\frac{\Delta\gamma}{\gamma}\right)\left(\frac{\omega^2}{\omega_0^2}-1\right)-2\frac{\Delta\gamma}{\gamma}+\sigma\right\}-\left(\frac{\Delta\gamma}{\gamma}\right)\frac{(\sigma+1)^2}{\sigma}$$

$$-\left(\frac{\Delta M}{M_1}\right)\left(\frac{\Delta\gamma}{\gamma}\right)\frac{\omega^2}{\omega_0^2}\left(\left(\frac{\omega^2}{\omega_0^2}-\frac{1}{\sigma}\right)\Big/\left(\frac{\omega^2}{\omega_0^2}-1\right)\right)^{1/2}\frac{3}{\sqrt{\sigma}}\left\{\sigma\left(\frac{\omega^2}{\omega_0^2}-1\right)-1\right\}^2I(0)\Bigg], \tag{47}$$

$$F_S^*=\left(1+\frac{\Delta\gamma}{\gamma}\right)+\frac{\Delta\gamma}{\gamma}\left(1+\frac{\Delta M}{M_1}\right)\frac{\omega^2}{\omega_0^2}+\left(\frac{\Delta M}{M_1}-\frac{\Delta\gamma}{\gamma}\right)\frac{\omega^2}{\omega_0^2}3(\sigma)^{1/2}\left(\left(\frac{\omega^2}{\omega_0^2}-\frac{1}{\sigma}\right)\Big/\left(\frac{\omega^2}{\omega_0^2}-1\right)\right)^{1/2}I(0)$$

$$-\frac{\Delta\gamma}{\gamma}\left(1+\frac{\Delta M}{M_1}\right)\frac{\omega^2}{\omega_0^2}3(\sigma)^{1/2}\left[\left(\frac{\omega^2}{\omega_0^2}-\frac{1}{\sigma}\right)\left(\frac{\omega^2}{\omega_0^2}-1\right)\right]^{1/2}I(0). \tag{48}$$

TABLE I. Results for various infrared impurity lines in KBr.

	Observed[a] resonance frequency (cm^{-1})	ω/ω_m	$\Delta\gamma/\gamma$ Calculated[b]
KBr:Li^6Br	17.9	0.158	−0.994
KBr:Li^7Br	16.3	0.144	−0.995
KBr:Ag^{108}Br	33.5	0.296	−0.594

[a] Reference 1.
[b] Sievers and Takeno (Ref. 1) have also estimated the impurity force constants for Li impurity in KBr, on the basis of a simple-cubic-lattice model. Their estimate is in reasonable agreement with ours even though their model is somewhat unrealistic.

Here ω_0 is the lowest frequency of the optical branch, given by

$$\omega_0^2=6\gamma/M_2$$

and

$$\sigma=M_2/M_1; \tag{49}$$

$$I(0)=2\gamma g_0^*, \tag{50}$$

$$g_0^*=(\mathbf{M}^*\omega^2-\mathbf{\Phi})_{0,0}^{-1}=\frac{1}{N}\sum_{\mathbf{k}}\frac{1}{M^*\omega^2-M^*\omega^2(\mathbf{k})}, \tag{51}$$

and the dispersion relation is given by

$$M^*\omega^2(\mathbf{k})=6\gamma-2\gamma(\cos k_1+\cos k_2+\cos k_3). \tag{52}$$

In obtaining the above expression the following relations between the Green's functions were used:

$$6\gamma g_1^*=1-ag_0^*, \tag{53}$$

$$ag_1^*+\gamma(g_0^*+4g_{11}^*+g_2^*)=0, \tag{54}$$

where

$$g_1^*=g_{0,0,0;\pm1,0,0}^*=g_{\pm1,0,0;0,0,0}^*, \tag{55}$$

$$g_2^*=g_{\pm1,0,0;\mp1,0,0}^*, \tag{56}$$

$$g_{11}^*=g_{\pm1,0,0;0,\pm1,0}. \tag{57}$$

CONCLUSION

Since extensive tables of Green's functions for these lattice models are now available,[7,11] it is easy to plot the line-shape function. In both the cases we have considered, a pronounced resonance peak appears in the low-frequency region for large $\Delta M/M$. This is essentially the Brout-Visscher resonance arising out of peaking in the density of states in the low-frequency region in the impure crystal. But resonances also appear for lighter defects if the force constants are adequately diminished.

This analysis can be fitted to some experimental data that have been obtained by Sievers[1] and subsequently analyzed by Sievers and Takeno on the far-infrared spectrum of KBr with Li and Ag impurities. For KBr, $\sigma=2$ and the reststrahlen wavelength is 88.3 μ. Table I gives the experimental data on the resonances and our values for the parameter $\Delta\gamma/\gamma$ for the few impurities for which data exist. The value of the parameter $\Delta\gamma/\gamma$ is obtained by adjusting it until the following equation is satisfied:

$$ReF_S^*=0.$$

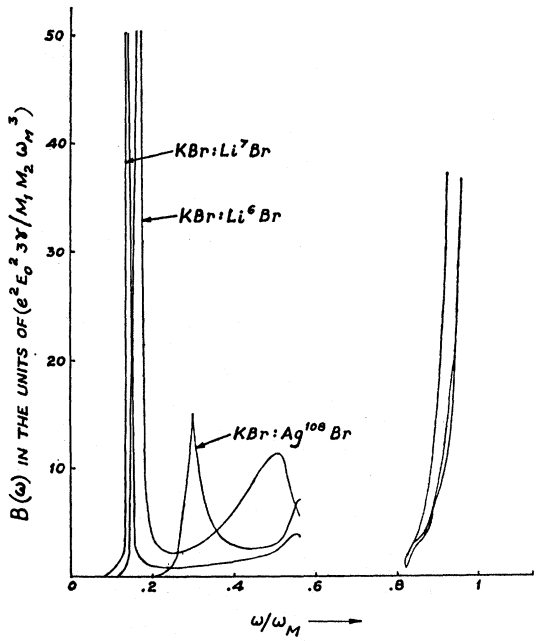

FIG. 1. $B(\omega)$ is plotted in units of $e^2E_0^2 3\gamma/M_1M_2\omega_m^3$ against ω/ω_m for KBr:Li^6Br, KBr:Li^7Br, and KBr:Ag^{108}Br.

The absorption line shapes of KBr with Li^6, Li^7, and Ag^{108} impurities are plotted against ω/ω_n in Fig. 1. The estimates of the perturbation parameters obtained here are in reasonable agreement with those obtained by Sievers and Takeno. It must be mentioned, however, that as in other aspects of lattice dynamics, the proper choice of the lattice model is the most difficult aspect of this problem. The line-shape analysis on the basis of the above approach is more in the nature of a phenomenological description of the situation than a detailed quantitative treatment. It may be noticed that discrete frequencies associated with localized modes outside the bands will absorb giving a δ-function line shape, arising out of the pole of $G(0,0)$ in Eqs. (16) and (24) outside the band. This line will be broadened due to anharmonic effects.

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