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Model Potential Calculation of the Raman Tensor for Be, Mg, and Zn[†]

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A model potential calculation of the first derivative of the electronic polarizability with respect to an atomic displacement for Be, Mg, and Zn is presented. The magnitudes of these derivatives, which govern the intensity of the first-order Raman effect in the corresponding crystals at the argon-ion laser wavelength of 4880 Å, are 39.7 Å^2 for Be, 11.2 Å^2 for Mg, and 18.9 Å^2 for Zn. The dependence of the real and imaginary parts of the polarizability derivative on the frequency of the incident light has also been calculated for these crystals.

Recently, Parker, Feldman, and Ashkin[1] have reported observing first-order Raman scattering from optical phonons in the hexagonal metals Be, Mg, and Zn. A theory of the Raman effect in metals has been presented by Mills, Maradudin, and Burstein.[2] However, in this theory the first derivative of the electronic polarizability of the metal with respect to a nuclear displacement, which governs the intensity of the Raman scattering of light by one-phonon processes, was left as a parameter of the theory.

In this paper we present a calculation of the first derivative of the electronic polarizability for an elemental hexagonal close-packed (hcp) metal and present results of the calculation for Be, Mg, and Zn.

The electronic polarizability of a crystal $P_{\alpha\beta}$ can be expanded in powers of the displacements of the atoms from their equilibrium positions as

$$P_{\alpha\beta}(\omega)=P^{(0)}_{\alpha\beta}(\omega)+\sum_{l\kappa\gamma} P_{\alpha\beta,\gamma}(\omega\,|\,l\kappa)u_{\gamma}(l\kappa)+\cdots\,, \qquad (1)$$

where ω is the frequency of the incident light, and $u_{\alpha}(l\kappa)$ is the α Cartesian component of the displacement of the κth atom in the lth primitive unit cell. We neglect the dependence of the electronic polarizability on the wave vector of the incident light. It is with the calculation of the $P_{\alpha\beta,\gamma}(\omega\,|\,l\kappa)$ that we are concerned in this paper.

If we divide $P_{\alpha\beta}$ by the volume of the crystal Ω, we obtain the dielectric susceptibility of the crystal

$$\chi_{\alpha\beta}(\omega)=\Omega^{-1}P^{(0)}_{\alpha\beta}(\omega)+\Omega^{-1}\sum_{l\kappa\gamma} P_{\alpha\beta,\gamma}(\omega\,|\,l\kappa)u_{\alpha}(l\kappa)+\cdots\,. \qquad (2)$$

Because of the translational periodicity of a crystal, $P_{\alpha\beta,\gamma}(\omega\,|\,l\kappa)$ is independent of the cell index l. In what follows we will denote this coefficient by $P_{\alpha\beta,\gamma}(\kappa)$, where to simplify the notation we suppress its explicit dependence on ω.

The translation vectors for crystals of the hcp structure are

$$\vec{a}=(\tfrac{1}{2}\sqrt{3}a,\ -\tfrac{1}{2}a,\ 0),\quad \vec{b}=(0,a,\ 0),\quad \vec{c}=(0,\ 0,\ c), \qquad (3)$$

where a and c are the two lattice parameters needed to describe the crystal structure. The Cartesian components of a general reciprocal-lattice vector are

$$G_x=(2G_1+G_2)2\pi/\sqrt{3a},\quad G_y=G_2 2\pi/a\ ,\quad G_z=G_3 2\pi/c\ , \qquad (4)$$

where G_1, G_2, G_3 are positive or negative integers.

It is convenient to choose the origin of coordinates midway between the two atoms in a primitive unit cell, so that the coordinates $\vec{x}(+)$ and $\vec{x}(-)$ of these two atoms are

$$\vec{x}(+)=(a/2\sqrt{3},\ 0,\ \tfrac{1}{4}c)=\vec{\tau}=-\vec{x}(-). \qquad (5)$$

It follows from infinitesimal translational invariance that, for crystals of the hcp structure,

$$P_{\alpha\beta,\gamma}(+)=-P_{\alpha\beta,\gamma}(-). \qquad (6)$$

In addition, from the transformation properties of $P_{\alpha\beta,\gamma}(+)$ when the crystal is subjected to one of the operations of its space group, it follows that this third-rank tensor has only one independent nonzero component for crystals of the hcp structure:

$$P_{xx,x}(+)=-P_{yy,x}(+)=-P_{xy,y}(+)=-P_{yx,y}(+). \qquad (7)$$

Combining these results we find that we can expand the change in the dielectric susceptibility due to atomic displacements $\delta\chi_{xx}(\omega)$ in the form

$$\delta\chi_{xx}(\omega)=\Omega^{-1}\sum_l P_{xx,x}(+)[u_x(l+)-u_x(l-)]\,, \qquad (8)$$

to first order in the displacements.

To simplify the calculations, we assume a displacement pattern of the form $\vec{u}(l+)=-\vec{u}(l-)=\vec{d}$, where $\vec{d}$ is independent of l. Such a displacement pattern describes a relative rigid-body displacement of the two sublattices with respect to each other, as in a $\vec{q}=0$ optical mode. It does not alter the periodicity of the crystal, just the structure of a primitive unit cell. The change in the susceptibility due to such a displacement pattern is therefore

$$\delta\chi_{xx}(\omega)=2\Omega_0^{-1}P_{xx,x}(+)d_x, \qquad (9)$$

where Ω_0 is the volume of a primitive unit cell.

We treat the metal as an electron gas which is only weakly perturbed by the periodic potential due to the positive ions. The bare-ion potential is represented by a weak model potential.

The Hamiltonian for the many-particle electron gas of the crystal perturbed by a spatially uniform electric field is

$$H = T_{\mathrm{el}} + V_{\mathrm{el-el}} + V_{\mathrm{el-ion}} + \frac{e}{mc}\sum_n \vec{p}_n \cdot \vec{A}_n(t), \tag{10}$$

where e is the magnitude of the electronic charge, m is the electronic mass, and $\vec{p}_n$ is the momentum operator of the nth electron. By calculating the expectation value of the total current operator, $-(e/m)\sum_n(\vec{p}_n + (e/c)\vec{A}_n)$, with respect to the time-dependent eigenstates of the Hamiltonian (10), one finds that the dielectric function is

$$\epsilon_{\alpha\beta}(\omega) = \delta_{\alpha\beta} - \frac{4\pi e^2 \mathfrak{N}}{m\omega^2\Omega}\,\delta_{\alpha\beta} - \frac{4\pi e^2}{m^2\omega^2\Omega} \times \sum_\mu \left\{ \frac{\langle 0|P_\alpha|\mu\rangle\langle\mu|P_\beta|0\rangle}{\mathcal{E}_0 - \mathcal{E}_\mu + \hbar\omega + i\hbar\epsilon} + \frac{\langle 0|P_\beta|\mu\rangle\,\langle\mu|P_\alpha|0\rangle}{\mathcal{E}_0 - \mathcal{E}_\mu - \hbar\omega - i\hbar\epsilon} \right\}, \tag{11}$$

where Ω is the crystal volume, $\mathfrak{N}$ is the number of valence electrons in the crystal, P_α is the α Cartesian component of $\sum_n \vec{p}_n$, and $\{|\mu\rangle\}$ and $\{\mathcal{E}_\mu\}$ are the time-dependent eigenstates and eigenvalues of the Hamiltonian (10) in the absence of the last term. The perturbation is turned on adiabatically with a factor $e^{\epsilon t}$.

Regarding the electron-ion interaction as a weak perturbation, we will expand $\epsilon_{\alpha\beta}(\omega)$ in powers of this interaction. We write the electron-ion interaction $V_{\mathrm{el-ion}}$ as

$$V_{\mathrm{el-ion}} = \sum_n \sum_{l\kappa} U(\vec{r}_n - \vec{x}(l\kappa) - \vec{u}(l\kappa)), \tag{12}$$

where $U(\vec{r})$ is the bare-ion potential, $\vec{r}_n$ is the position of the nth electron, and $\vec{x}(l\kappa)$ is the equilibrium position of the κth atom in the lth primitive unit cell. We may write this as

$$V_{\mathrm{el-ion}} = \sum_{\vec{q}n}\sum_{l\kappa} U(\vec{q})e^{-i\vec{q}\cdot\vec{x}(l\kappa)}e^{-i\vec{q}\cdot\vec{u}(l\kappa)}e^{i\vec{q}\cdot\vec{r}_n} = \sum_{\vec{q}n} V(\vec{q})e^{i\vec{q}\cdot\vec{r}_n}, \tag{13}$$

where $U(\vec{q})$ is

$$U(\vec{q}) = (1/\Omega)\int d^3r\, U(\vec{r})e^{-i\vec{q}\cdot\vec{r}}. \tag{14}$$

We denote by $\{|\mu)\}$ and $\{E_\mu\}$ the eigenstates and eigenvalues of the Hamiltonian containing only electron-electron interactions. These states are also eigenstates of P_α with eigenvalue $P_{\alpha\mu}$, and P_α acting on the ground state $|0)$ has eigenvalue zero. Omitting the terms which are unmodulated by atomic displacements, the dielectric function becomes

$$\epsilon_{\alpha\beta}(\omega) = \frac{4\pi e^2}{m^2\omega^2\Omega}\sum_{\vec{q}} \frac{P_{\alpha\mu}P_{\beta\mu}|(\mu|V(\vec{q})\sum_n e^{i\vec{q}\cdot\vec{r}_n}|0)|^2}{(E_\mu - E_0)} \times\left(\frac{1}{E_\mu - E_0 - \hbar\omega - i\hbar\epsilon} + \frac{1}{E_\mu - E_0 + \hbar\omega + i\hbar\epsilon}\right), \tag{15}$$

which is exact to second order in $V(\vec{q})$.

The longitudinal dielectric function of an interacting electron gas obtained from response to a test charge is[3]

$$\frac{1}{\epsilon(\vec{q},\omega)} = 1 - \frac{4\pi e^2}{q^2\Omega}\sum_\mu |(\mu|\sum_n e^{i\vec{q}\cdot\vec{r}_n}|0)|^2 \times\left(\frac{1}{E_\mu - E_0 - \hbar\omega - i\hbar\epsilon} + \frac{1}{E_\mu - E_0 + \hbar\omega + i\hbar\epsilon}\right). \tag{16}$$

By comparing Eqs. (15) and (16), we obtain for the real and imaginary parts of the dielectric function defined by $\epsilon_{\alpha\beta}(\omega) = \epsilon^{(1)}_{\alpha\beta}(\omega) + i\epsilon^{(2)}_{\alpha\beta}(\omega)$

$$\epsilon^{(1)}_{\alpha\beta}(\omega) = -\frac{1}{m^2\omega^4}\sum_{\vec{q}}|V(\vec{q})|^2 q^2 q_\alpha q_\beta \times \mathrm{Re}\left(\frac{1}{\epsilon(\vec{q},\omega)} - \frac{1}{\epsilon(\vec{q},0)}\right), \tag{17a}$$

$$\epsilon^{(2)}_{\alpha\beta}(\omega) = -\frac{1}{m^2\omega^4}\sum_{\vec{q}}|V(\vec{q})|^2 q^2 q_\alpha q_\beta\, \mathrm{Im}\left(\frac{1}{\epsilon(\vec{q},\omega)}\right). \tag{17b}$$

The result (17b) for $\epsilon^{(2)}_{\alpha\beta}(\omega)$ was obtained previously by Hopfield.[4] The contribution to the real and imaginary parts of the electronic susceptibility which is modulated by nuclear displacements is obtained by dividing Eq. (17) by 4π.

If we now consider the atomic-displacement pattern discussed previously, we may write $V(\vec{q})$ to first order in $\vec{d}$ as

$$V(\vec{q}) = \Delta(\vec{q})W(\vec{q})\,[\cos\vec{q}\cdot\vec{\tau} - \vec{q}\cdot\vec{d}\sin\vec{q}\cdot\vec{\tau}], \tag{18}$$

where $W(\vec{q}) = 2NU(\vec{q})$ and $\Delta(\vec{q})$ is equal to 1 if $(\vec{q})$ is a reciprocal-lattice vector, and zero otherwise. If we denote the real and imaginary parts of $P_{xx,x}(+)$ by P and Q, we have from Eq. (9), where $W(\vec{q}) = 2NU(\vec{q})$,

$$P = \frac{\Omega_0}{8\pi m^2\omega^4}\sum_{\vec{G}}|W(\vec{G})|^2 G^2 G_x^3 \sin 2\vec{G} \cdot \vec{\tau}\, \mathrm{Re}\left(\frac{1}{\epsilon(\vec{G},\omega)} - \frac{1}{\epsilon(\vec{G},0)}\right), \tag{19a}$$

$$Q = \frac{\Omega_0}{8\pi m^2\omega^4}\sum_{\vec{G}}|W(\vec{G})|^2 G^2 G_x^3 \sin 2\vec{G} \cdot \vec{\tau}\, \mathrm{Im}\left(\frac{1}{\epsilon(\vec{G},\omega)}\right). \tag{19b}$$

In the evaluation of these sums for Be, Mg, and Zn, we used the dielectric function calculated by Lindhard[5] on the basis of the random-phase approximation. The quantities $W(\vec{q})$, which were calculated using the bare-ion part of the model potential given by Animalu and Heine,[6] are tabulated in Table I. The constants used are shown in Table II.

The values for P and Q were calculated for Be, Mg, and Zn as functions of ω for $0 \leq \hbar\omega \leq 10$ eV. For small values of ω, $P \sim 1/\omega^2$ and $Q \sim 1/\omega^3$.

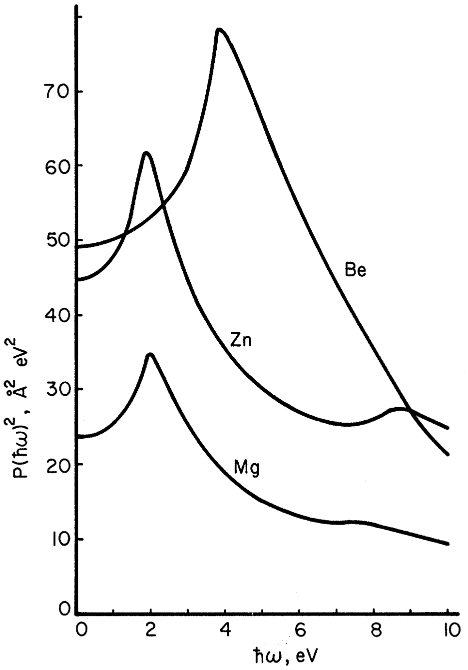

FIG. 1. Variation of $P(\hbar\omega)^2$ with incident-photon energy for Be, Zn, and Mg.

Therefore, we plot $P(\hbar\omega)^2$ and $Q(\hbar\omega)^3$ in Figs. 1 and 2. It is noted that a sharp break occurs in these curves in the region of 2–4 eV. The real part of the Lindhard dielectric function has an inflection point with infinite slope at a point where the photon energy equals the kinetic energy difference between an electron of wave vector $q - q_F$ and an electron of wave vector q_F, where q_F is the magnitude of the Fermi wave vector. This property of the dielectric function causes the contribution from each reciprocal-lattice vector to have a sharp break in the curve at this photon energy. As it happens, the breaks noted come from the next-nearest-neighbor contribution. For Mg and Zn, a slight peak from the third-neighbor contribution is also evident near 8 eV.

TABLE I. Model potential parameters $W(\vec{G})$ used in the calculation of the Raman tensors for Be, Mg, and Zn (in Ry).

G_1, G_2, G_3	Be	Mg	Zn
1 0 0	0.073	0.012	0.006
1 0 1	0.105	0.040	0.049
1 0 2	0.062	0.042	0.082
1 0 3	−0.015	0.007	0.058
2 0 0	−0.021	0.001	0.026
2 0 1	−0.025	−0.003	0.021
2 0 2	−0.026	−0.008	0.008
1 0 4	−0.020	−0.009	0.015

TABLE II. Constants used in the calculation of Raman tensors for Be, Mg, and Zn.

	Z	a(Å)	c(Å)
Be	2	2.287	3.583
Mg	2	3.203	5.196
Zn	2	2.6585	4.9342

We can compare our theoretical results with the experimental results of Parker *et al.*,[7] who found that at a laser frequency of 4880 Å (2.54 eV)

$$|P+iQ|_{\text{Be}}/|P+iQ|_{\text{Si}} \cong 0.08-0.13 \text{ (expt).} \qquad (20)$$

In another paper,[8] the present authors have made an *ab initio* pseudopotential calculation of the Raman tensors for diamond, silicon, and germanium. The value of $P\,(Q=0)$ for silicon at a laser frequency of 4880 Å was found to be 51.5 Å^2. Using the values from Figs. 1 and 2, $|P+iQ|_{\text{Be}} = 39.7$ Å^2, and the corresponding theoretical value of the ratio in Eq. (20) is

$$|P+iQ|_{\text{Be}} \,/\, |P+iQ|_{\text{Si}} = 0.77 \text{ (theor).} \qquad (21)$$

This differs from the experimental value by about a factor of 6. The values of $|P+iQ|$ for Mg and Zn are 11.2 Å^2 and 18.9 Å^2, respectively.

In assessing possible sources of error in the present calculation, we note that in carrying out the expansion of $\epsilon_{\alpha\beta}(\omega)$ in Eq. (15) to second order in $V(\vec{G})$, we have neglected the terms of higher order in $V(\vec{G})$. A calculation of the contributions to P and Q at an incident frequency of 2.5 eV which are of third order in $V(\vec{G})$ shows that they are smaller than

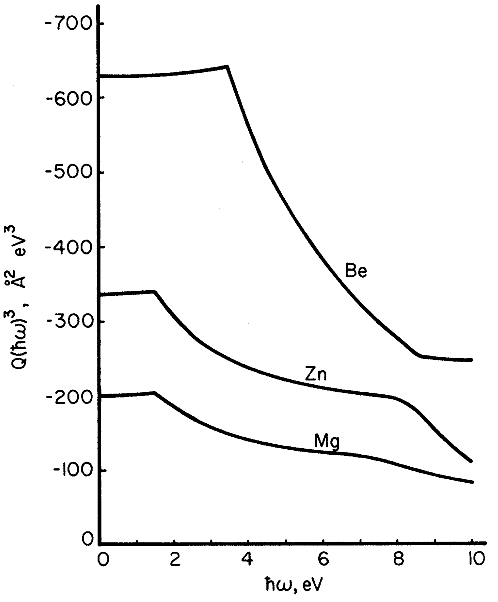

FIG. 2. Variation of $Q(\hbar\omega)^3$ with incident-photon energy for Be, Zn, and Mg.

the contributions of second order by a factor of $0.1|V(\vec{G})|_{\max}/E_F$, where E_F is the Fermi energy. This factor is less than 0.01.

It should be noted that in the sums in Eqs. (19) the terms corresponding to the first two or three nearest-neighbor reciprocal-lattice vectors dominate. As it turns out, the contribution of the nearest-neighbor reciprocal-lattice vector comes in with a sign opposite to that of the next two nearest neighbors due to the factor $\sin(2\vec{G}\cdot\vec{\tau})$. Also, for each metal the magnitude of the nearest-neighbor reciprocal-lattice vector is close to the value of q at which $W(q)$ has its first zero. As a result, comparatively small changes in the bare-ion model potential can significantly affect the contributions to P and Q, even to the extent of changing the signs of these contributions, decreasing thereby the value of $|P+iQ|$.

The principal source of error in the present calculations is probably to be found in the choice of a bare-ion model potential. It is possible that a different choice from that made here could lead to an improvement in the agreement between theory and experiment. Nevertheless, it is still gratifying that the simple calculation described here is capable of yielding values of the Raman tensors of Be, Mg, and Zn which are in order-of-magnitude agreement with such experimental values as exist.

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Effect of Weak Surface Autocorrelation on the Size Effect in Electrical Conduction

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Correlation between points on a conductor surface may be important in explaining the relatively large specularity parameters attributed to measurements in single-crystal samples. An expression for the size effect in the electrical conductivity is obtained that takes into account the effect of weak surface autocorrelation. The expression shows that, as expected, the correlation increases the electrical conductivity. It also shows that even an angle-dependent specularity parameter may not be an adequate description in the sense of the Fuchs model. Numerical estimates are given for the size effects due to surface roughness and autocorrelation. These are explained in terms of the competing effects of flux conservation and surface asperity slopes.

Most descriptions of the effect of surface scattering of conduction electrons have employed the constant specularity parameter p as introduced by Fuchs.[1] It has generally been recognized that a constant p is not likely to provide a realistic description of this process, except under simplifying conditions.[2] If the surface scattering is due to random surface charges, the specularity parameter may depend on the angle of incidence of the electron's wave vector and the surface and may also differ from the magnitude expected on the basis of the reflection coefficient.[3] Surface roughness also is expected to produce an angle-dependent specularity parameter.[4] In addition, the degree of correlation between the heights of various points on the surface should have an effect on the detailed nature of the portion of the scattered flux usually described as "diffuse." With increasing autocorrelation of the surface heights, the "diffuse" flux should have a narrower distribution about the spec-