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Theory of angle-resolved photoemission from the bulk bands of solids. III. Effects of intra-atomic and interatomic electron-phonon interactions

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In this third paper of a series, the influence of phonons upon the angle-resolved spectra of electrons photoemitted from the bulk bands of solids is considered. When a tight-binding formalism is used to describe the electronic states of solids, it is possible to divide the electron-phonon interaction into terms that mix orbitals located on the same site (intra-atomic) and on different sites (interatomic). The intra-atomic interactions can be treated simply by using a basis set in which the atomic orbitals follow the displacement of the atoms. The effects of this intra-atomic interaction are to weaken the usual k-selection rules in a manner discussed in previous works. When the initial states only are perturbed by the interatomic electron-phonon interaction, the primary modification of the angle-resolved photoelectron spectra is a broadening and shifting of the features observed at low temperatures while the conservation of k and polarization selection rules appear to remain essentially intact. When the final states are modified by the interatomic electron-phonon interaction, the direct k-conserving component of the spectra decreases as the temperature increases, while an angle-averaged-like component increases. The electron-phonon interaction also decreases the mean free path of the photoelectron, thereby increasing the tendency of the spectra to resemble one-dimensional density of states. The form of the spectra expected in various cases is discussed.

I. INTRODUCTION

In previous papers in this series[1,2] and elsewhere[3-5] attention has been focused upon the development of a simple theory for describing the positions, shapes, and intensities of peaks in the photoelectron spectra of the bulk bands of solids for arbitrary angles of emission, polarization, and photon energies. This theory was derived for the perfect crystal, which in reality does not exist owing to the disorder induced by vibrational displacements of the atoms.

The influence of phonons in modifying the optical and transport properties of solids has been discussed in several previous works.[6-9] In photoemission from localized states, e.g., core levels or molecular levels, it has been shown that the hole potential left behind by the photoelectron can excite vibrational modes.[10,11] Such a mechanism is not expected to be important in photoemission from extended bulk or surface bands, where the hole potential is much weaker. Very few experimental or theoretical works have dealt with the effects of lattice vibrations expected in the photoemission spectra from the states of solid surfaces.

Bauer *et al.*[12] attributed the large temperature dependences of the peaks in the angle-resolved photoemission spectra of the silver halides to phonon-induced changes of the energies of the initial states. Using a tight-binding formalism, they concluded that the electron-phonon interaction should be largest for materials having ionicities in a certain range. Williams *et al.*[13] observed that the angle-resolved photoelectron spectrum of Cu obtained for $h\nu = 40$ eV begins to resemble the total density of states as the temperature is increased to 800 °C. They interpreted their results in terms of a model, suggested by Shevchik,[14] that predicts the weakening of k conservation in the optical ionization matrix element as the temperature and photon energy increase. Heimann and Neddermeyer[15] observed the peaks in the angle-resolved photoelectron spectrum of Au to broaden and to shift with increasing temperature and suggested that relaxation of momentum conservation could account for some of the observed changes. Grandke and Cardona[16] recently observed a broadening of the angle-resolved photoelectron spectra of PbS and PbSe and interpreted their results in terms of an initial-state energy broadening due to electron-phonon interactions, similar to that proposed by Bauer *et al.*[12]

Caroli *et al.*[17] used a Green's function technique to discuss emission and absorption of phonons by the photoelectron. Sayers and McFeely,[18] using a perturbative approach, concluded that phonons have very little effect upon weakening momentum conservation in optical transitions in the x-ray regime, in disagreement with the previous analysis of Shevchik.[14]

In this third paper of a series the role of lattice vibrations in modifying the angle-resolved photoelectron spectra from the bulk bands of solids is discussed more completely than in previous works.[14] The structure of this paper is as follows: In Sec. II the electron-phonon interaction is divided into terms that affect atomic orbitals on the same site (intra-atomic) and orbitals on different sites (interatomic). In Sec. III the role of the intra-atomic electron-phonon interaction is briefly discussed. This interaction was already treated in a previous paper in some detail,[14] although there it was not explicitly identified as an intra-atomic interaction. In Sec. IV we show that when the interatomic electron-phonon interaction modifies the initial states, and not the final states, the only observable change in the angle-resolved photoelectron spectra should be a broadening and shifting in energy of the features observed at very low temperatures; the conservation of k and the dipole selection rules are not modified significantly. However, when the final state is scattered by the interatomic electron-phonon interaction, the spectra observed at low temperatures exhibit diminished conservation of the component of momentum perpendicular to the surface and begin to decrease in intensity as the temperature increases, whereas a spectrum that resembles the angle-averaged photoelectron spectra rises in intensity. In Sec. V we discuss the situations in which the various predicted effects are to be observed.

II. INTRA-ATOMIC AND INTERATOMIC VIBRATION-INDUCED INTERACTIONS

The change in the one-electron potential of a monoatomic solid induced by the instantaneous displacement of the atoms can be written as[6]

$$\Delta V(r)=\sum_{l} V(\vec{r}-\vec{R}_l-\delta\vec{R}_l)-V(\vec{r}-\vec{R}_l)\,, \tag{1}$$

where $V(r)$ is the atomic potential and $\delta\vec{R}_l$ is the displacement of the atom away from its equilibrium position $\vec{R}_l$. The use of a tight-binding formalism to describe the electronic states of the solid[6] makes it possible to separate changes in the potential induced by the displacement of the atoms into intra-atomic and interatomic terms. We define the intra-atomic and interatomic electron-phonon interactions to correspond to the matrix elements of $\Delta V(r)$ between atomic orbitals on the same site and different sites, respectively.

III. INTRA-ATOMIC EFFECTS

The vibration-induced change in the potential, becoming very large near the atomic cores, can mix together Bloch wave functions, valid for the perfect crystal, extending over a considerable range of energy. It is clear that the change in the potential near the atomic cores leads to large matrix elements between orbitals centered on the same site and, therefore, makes the dominant contribution to the intra-atomic electron-phonon interaction. Since this interaction is large near the atomic cores, it is not efficiently treated with usual perturbation techniques. (In fact, the atomic potential cannot even be expanded in a convergent Taylor series in the displacements for $|\vec{r}|<|\delta\vec{R}_l|$.) The proper way to treat the intra-atomic electron-phonon interaction can be deduced from consideration of the displacement of an isolated atom. It is clear that, since the atomic potential is large and the electron has a small mass, the atomic orbitals follow the displacement of the atomic potential, and no change in energy occurs.[19] A perturbative approach to describe this trivial displacement of a single atomic orbital would require several atomic orbitals centered about the original equilibrium site. Since the change in the energies of the electronic states due to the intra-atomic interaction is much smaller than the change due to the interatomic interaction (which will be treated in Sec. IV), the shifts in the energies will be neglected in this section.

The most important effects of the intra-atomic interactions are taken into account by using a basis set of the form[14,20]

$$|k\rangle_d=\sum_{l}\exp[i\vec{k}\cdot(\vec{R}_l+\delta\vec{R}_l)]\phi_{\vec{k}}(\vec{r}-\vec{R}_l-\delta\vec{R}_l) \tag{2}$$

to describe both the initial and final states. With the wave functions written in the above form the atomic orbitals $\phi_{\vec{k}}(r)$ are constrained to follow the motion of the atoms. The form of the wave function is entirely consistent with the observation made in x-ray scattering that the atomic x-ray form factor which is the Fourier transform of the electronic charge density, follows the movement of the nuclei.[21,22] While this is true for core electrons and the part of the valence electrons near the core, it is less true for the outer regions of the valence orbitals, which are also constrained by the neighboring environment. It is not clear whether the vibrational displacement ought to appear in the phase factor in Eq. (2) for Bloch waves describing valence electrons. At high energies, however, where the final state is well approximated by augmented plane waves, the displacement must appear, for a large amount of kinetic energy must be expended to make the phase otherwise.

It was shown that the photoionization cross section per atom between an initial state $|k_i\rangle_d$ and a plane-wave final state (or an augmented plane-wave) of extended momentum $\vec{k}_f$ takes the form[14]

$$\begin{aligned}|\langle\vec{k}_f|\vec{p}\cdot\vec{\epsilon}|k_i\rangle_d|^2 &=\sigma(\vec{k}_f,\vec{k}_i,\vec{\epsilon})[\delta(\vec{k}_f-\vec{k}_i)e^{-W(\vec{k}_f,\vec{k}_i)})],\\ &\quad +N^{-1}(1-e^{-W(\vec{k}_f,\vec{k}_i)})]\,,\end{aligned} \tag{3a}$$

$$\sigma(\vec{k}_f,\vec{k}_i,\vec{\epsilon})=\int d\vec{r}e^{-i\vec{k}_f\cdot\vec{r}}\vec{p}\cdot\vec{\epsilon}\phi_{\vec{k}_i}(\vec{r})\,, \tag{3b}$$

where $\sigma(\vec{k}_f, \vec{k}_i, \vec{\epsilon})$ is the photoionization cross section of the atomic orbital $\phi_{\vec{k}_i}(r)$, $\vec{k}_f$, and $\vec{k}_i$ are the reduced momenta of the initial and final states, and

$$W(\vec{k}_f, \vec{k}_i) = \langle [(\vec{k}_f - \vec{k}_i) \cdot \delta \vec{R}_l]^2 \rangle \, .$$

When an augmented plane-wave final state is used, $\sigma(\vec{k}_f, \vec{k}_i, \vec{\epsilon})$ obeys atomic dipole selection rules, as was discussed in paper I of this series.[1] The first term in brackets in Eq. (3a) corresponds to direct momentum-conserving transitions reduced in strength by a Debye-Waller factor, and the second (thermal-diffuse) term corresponds to indirect transitions in which k conservation is almost totally relaxed.[14] The second term comes about from the inability of the initial and final states to maintain a definite phase with respect to one another owing to the random displacements of the atoms. The derivation of (3a) is exact except for the neglect of two effects: correlation of displacements of different atoms (which gives a weak q dependence to the thermal-diffuse cross section), and time-dependent displacement correlations (which give rise to a weak inelasticity). Neglecting for now the inelastic processes, we find as before that the intensity of electrons emitted in the final state $|\vec{k}_f\rangle$ is

$$I(\vec{k}_f, \vec{\epsilon}, \hbar\omega) = N \sum_{\vec{k}_i} \sigma(\vec{k}_f, \vec{k}_i, \vec{\epsilon}) \delta(E(\vec{k}_f) - E(\vec{k}_i) - \hbar\omega) \times [\delta(\vec{k}_f - \vec{k}_i) e^{-W(\vec{k}_f, \vec{k}_i)} + N^{-1}(1 - e^{-W(\vec{k}_f, \vec{k}_i)})] \, , \tag{4}$$

where N is the total number of atoms contributing to the spectrum. The first term in the square brackets yields a component of the spectrum which corresponds to direct momentum-conserving transitions, while the second term, corresponding to completely indirect transitions, yields a component that looks like the total density of initial states modulated by atomic photoionization cross sections.[14] The direct-transition term dominates when $W(\vec{k}_f, \vec{k}_i) < 1$, and the density-of-states term dominates when $W(\vec{k}_f, \vec{k}_i) > 1$. The intra-atomic effects do not go away as the momentum of the final state increases, but actually become more important. In fact, as the photon energy increases, the present theory becomes more valid, since the regions closer to the atomic cores make the primary contribution to the photoionization cross section.[14] The intra-atomic effect is still present even in the limit that the final state is not perturbed by the crystal potential but is a plane wave. For this reason we can regard the intra-atomic effect as associated primarily with the initial electronic state.

It was also shown that, when the time dependence of the motion of the atom is taken into account, the spectra become broadened in energy due to a Doppler-like effect.[14,23] However, this energy-broadening mechanism is usually small in comparison to the effect that the interatomic electron-phonon interaction has upon the initial state.[12] Nowhere in this analysis does the strength of the atomic potential enter. The assumption that the atomic orbitals follow the nuclear core is equivalent to the assumption that the interatomic electron-phonon interaction is infinite. It is doubtful whether perturbative methods will succeed in reproducing the effect of intra-atomic interactions produced here, since they arise from the very singular nature of the atomic potential near the core.

The present analysis must be regarded as in disagreement with the analysis of Sayers and McFeely,[18] who concluded that the effects of phonons are not important in the x-ray photoemission regime. We shall argue later that Sayers and McFeely[18] treated the interatomic part of the electron-phonon interaction, which gives different effects from the intra-atomic mechanism treated here.

When the intra-atomic effect is treated quantum mechanically, it can be seen that the Debye-Waller factor arises from absorption and emission of phonons due to the momentum recoil of the atomic site when the electron is ejected. The theory presented previously[14] and presently, however, does give the correct quantum-mechanical expectation values for the intensities.

IV. EFFECTS OF INTERATOMIC ELECTRON-PHONON INTERACTIONS

A. Modification of electronic states

In the unperturbed solid the interatomic interaction induced by the crystal potential gives rise to the formation of energy bands and corresponding Bloch wave functions.[6] The changes in the interatomic interactions induced by phonons are weak enough to be treated, in principal, with perturbation theory. It is also reasonable to approximate the change in the potential in the region between the atoms by the first Taylor expansion term linear in the displacements. Since the interatomic electron-phonon interaction is small, it can mix appreciably only the Bloch wave functions of the perfect crystal that have nearly the same energy, i.e., it induces primarily intraband mixing.

Although the electron-phonon interaction is changing dynamically with time, the photoemission process, being first, takes a snapshot of the system with the electronic states in equilibrium with the disordered lattice. Therefore, we choose to use the eigenfunctions of the static but disordered lattice rather than a time-dependent formalism to describe the effects of the interatomic electron-phonon interaction. This assumption makes it impossible to account for the frequencies of the phonons, which, as we shall see, are small compared to the energy shifts induced by the electron-phonon interactions.[12]

The modified states (either initial or final) of the distorted lattice, $|s\rangle$, are assumed to be a linear combination of the Bloch states of the *undistorted lattice*, $|\vec{k}\rangle$, or

$$|s\rangle = \sum_{\vec{k}} a_s(\vec{k})|\vec{k}\rangle \,. \tag{5}$$

We presently use the basis set $|\vec{k}\rangle$, in which the atomic orbitals remain at the perfect lattice positions, as opposed to the distorted basis given in Eq. (2), in order to isolate the effects of the interatomic electron-phonon interaction upon the angle-resolved photoelectron spectra. Since the electron-phonon interaction contains terms that can connect all states within the Brillouin zone, the $a_s(\vec{k})$ is nearly uniformly distributed over all degenerate states in the Brillouin zone. This means that the k quantum number is no longer meaningful for describing the stationary states of the infinite, distorted system. The phase of $a_s(\vec{k})$ depends upon the specific distortion of the system, and therefore we expect that, when averaged over several sets of distortions occurring during the time of the measurement of the angle-resolved photoelectron spectra,

$$\langle a_s(\vec{k})^* a_{s'}(\vec{k}')\rangle = |a_s(\vec{k})|^2 \delta_{ss'} \delta_{\vec{k}\vec{k}'} \,. \tag{6}$$

From Green's-function methods[24] it has been shown that

$$\sum_s |a_s(\vec{k})|^2 \delta(E(s) - E) = \frac{\Sigma_2(\vec{k})}{[E - E(\vec{k}) - \Sigma_1(\vec{k})]^2 + [\Sigma_2(\vec{k})]^2} \,, \tag{7}$$

where

$$\Sigma_1(\vec{k}) = \sum_{\vec{k}'} \frac{|\Delta V_{\vec{k}\vec{k}'}|^2}{E(\vec{k}) - E(\vec{k}')} \,, \tag{8}$$

$$\begin{aligned}\Sigma_2(\vec{k}) &= \pi \sum_{\vec{k}'} |\Delta V_{\vec{k}\vec{k}'}|^2 \delta(E(\vec{k}) - E(\vec{k}')) \\ &\approx \pi \langle \Delta V^2 \rangle \rho(E(\vec{k})) \,,\end{aligned} \tag{9}$$

$\Delta V_{\vec{k}\vec{k}'}$ is the interatomic electron-phonon interaction connecting the two states, and $\rho(E(\vec{k}))$ is the density of electronic states at energy $E(\vec{k})$. Equation (7) shows that the state $|\vec{k}\rangle$ becomes distributed over stationary states of the perturbed system, $|s\rangle$, the peak of this distribution being shifted in energy by amount $\Sigma_1(\vec{k})$ from the position occurring in the perfect lattice, and the width increasing to $\Sigma_2(\vec{k})$. For further details of the modification of the electron states by phonons the reader is referred to the recent paper by Allen.[25]

B. Initial-state effects

We now consider the changes in the angle-resolved photoemission spectra occurring when the interatomic electron-phonon interactions modify the wave functions of the initial states only. For simplicity we assume that, as in Paper I of this series, there is only one single final state $|\vec{k}_f\rangle$, unmodified by the phonons, that couples at the surface to the plane-wave state $|\vec{K}_f\rangle$ propagating in the vacuum in the direction of the analyzer.

The intensity of electrons photoemitted into this state from initial states $|\vec{k}_i\rangle$ of the perfect crystal is

$$\begin{aligned}I(\vec{k}_f, \vec{\epsilon}, \hbar\omega) = \sum_{\vec{k}_i} & |\langle \vec{k}_f | \vec{p}\cdot\vec{\epsilon} | \vec{k}_i \rangle|^2 \\ & \times \delta(E(\vec{k}_f) - E(\vec{k}_i) - \hbar\omega) \,.\end{aligned} \tag{10}$$

In the disordered lattice the spectra can be written in the same form, except that the initial states are those of the modified system,

$$\begin{aligned}I(\vec{k}_f, \vec{\epsilon}, \hbar\omega) = \sum_{s} & |\langle \vec{k}_f | \vec{p}\cdot\vec{\epsilon} | s \rangle|^2 \\ & \times \delta(E(\vec{k}_f) - E(s) - \hbar\omega) \,.\end{aligned} \tag{11}$$

Using Eq. (5) to express $|s\rangle$ in terms of the states $|k\rangle$, performing the ensemble average over $a_s(\vec{k})$, and using Eq. (7), we find that the time-averaged photoemission spectrum is

$$\begin{aligned}\langle I(\vec{k}_f, \vec{\epsilon}, \hbar\omega)\rangle = \sum_{\vec{k}_i} & |\langle \vec{k}_f | \vec{p}\cdot\vec{\epsilon} | \vec{k}_i \rangle|^2 \\ & \times \Delta(E(\vec{k}_f) - E(\vec{k}_i) - \hbar\omega) \,,\end{aligned} \tag{12}$$

where

$$\Delta(E - E(\vec{k}_i) - \hbar\omega) = \frac{\Sigma_2(\vec{k}_i)}{[E - E(\vec{k}_i) - \hbar\omega - \Sigma_1(\vec{k}_i)]^2 + [\Sigma_2(\vec{k}_i)]^2} \,. \tag{13}$$

Comparison of Eqs. (10) and (12) reveals that the spectra for the perfect and disordered crystals are very similar. The optical-transition-matrix elements appearing in the summation are identical for the two cases. This means that the states contributing to the spectra in the perfect crystal are the basis functions that continue to contribute in the disordered lattice. The angle-resolved photoelectron spectrum in this case represents the spectral distribution of this set of basis functions projected over the modified states $|s\rangle$. Other regions of the Brillouin zone that do not contribute when perfect order exists show up in the spectra indirectly through the tails of the function $\Delta(E)$, where the density of states is mirrored by a fraction $|\Delta V_{\vec{k}\vec{k}'}|^2/W^2$, where W is the width of the band. We estimate that typically at room temperature the density-of-states-like portion of the spectrum is ~1%. Since such contributions, which can be regarded as indirect transitions, occur at levels that are barely observable in angle-resolved photoemission experiments, it can be concluded that k conservation and dipole selection rules do not appear to be modified significantly by this mechanism. [This is in contrast to the effects of the intra-atomic interaction discussed previously,[14] in which matrix elements in Eq. (12) are modified directly.] The primary observable effect of the interatomic electron-phonon interaction acting upon the initial states is a broadening and a shifting of the peaks from the positions observed at low temperatures. Since the broadening and shifting of the peaks is strictly an initial-state effect, it is independent of the energy of the final state. The effect discussed in this section is a more formal statement of the mechanism first suggested by Bauer *et al.*[12] However, the conclusions made here are completely independent of the nature of the final state, be it free-electron-like or otherwise.

C. Final-state effects

In this section we consider the form of the angle-resolved photoelectron spectra expected when the final and the initial states are modified by the interatomic electron-phonon interaction. The probability amplitude of finding the photoelectron excited from some initial state $|\vec{k}_i\rangle$ inside of the solid is given by

$$|PE\rangle_i = \sum_s |s\rangle\langle s|\vec{p}\cdot\vec{\epsilon}|\vec{k}_i\rangle\delta(E(\vec{K}_f) - E(s)) \times\delta(E(\vec{K}_f) - E(\vec{k}_i) - \hbar\omega)\,. \tag{14}$$

We use $\vec{K}_f$, the momentum of the electron outside of the solid, as the index for the final-state energy. Since the eigenstates of the disordered lattice contain momentum components distributed uniformly over the Brillouin zone, it does not, at first thought, seem possible that any angular dependence ought to be observed in the photoelectron spectra. Deep within the solid this is certainly true, but, as we now show, the boundary conditions imposed at the surface by the photoemission experiment cause an angular dependence to be observed.

To determine the intensity of electrons seen in the analyzer, one must consider the sum of the amplitudes that each state $|s\rangle$ makes. At the surface each state $|s\rangle$, which is represented in terms of Bloch states $|\vec{k}\rangle$, must match with a plane-wave basis set describing the electrons in the vacuum. The primary function of the electron velocity analyzer is to select a particular plane-wave state propagating in the direction of the analyzer. The probability amplitude of finding the photoelectron in the plane-wave state of momentum $|\vec{K}_f\rangle$ outside of the surface is approximately given by the projection

$$\begin{aligned} M(\vec{K}_f) &= \langle\vec{K}_f|PE\rangle_i \\ &= \sum_s \langle\vec{K}_f|s\rangle_p\langle s|\vec{p}\cdot\vec{\epsilon}|\vec{k}_i\rangle\delta(E(\vec{K}_f) - E(s)) \\ &\quad\times\delta(E(\vec{K}_f) - E(\vec{k}_i) - \hbar\omega)\,. \end{aligned} \tag{15}$$

The above approximation is equivalent to the assumption that the transmission amplitudes for the passage of the photoelectron through the surface are unity. As discussed in Paper I of this series,[1] this should be the case when the wavelength of the photoelectron is on the order of the width of the surface potential. The subscript p on the first matrix element in the above sum indicates that the integration is over the surface plane, and not over all space.

By inspection of Eq. (15) we find that the single final state inside of the solid that yields the correct probability amplitude of emission into the plane-wave state $|\vec{K}_f\rangle$ is

$$\langle s_f| = \sum_s \langle\vec{K}_f|s\rangle_p\langle s|\delta(E(\vec{K}_f) - E(s))\,. \tag{16}$$

The above linear combination of states is precisely the sum that one would put together to make the wave function immediately inside of the solid look like the plane wave just outside of the solid. As the distance inside of the solid increases, $|s_f\rangle$ begins to look less like the plane wave outside and more like a combination of plane waves propagating in all directions. Expressing $|s_f\rangle$ in terms of the wave functions for the ordered crystal, we find

$$\langle s_f| = \sum_s \sum_{\vec{k}\vec{k}'} \langle\vec{K}_f|\vec{k}\rangle_p a_s(\vec{k})a_s^*(\vec{k}')\langle\vec{k}'| \times\delta(E(\vec{K}_f) - E(s))\,. \tag{17}$$

We now consider whether there is a coherent part of the final-state wave function that survives an averaging over the phases of $a_s(\vec{k})$. Performing this average as before for the initial state, we find that the coherent part of the final state is

$$\begin{aligned} \langle s|_{\text{coh}} &\equiv \langle\langle s_f|\rangle \\ &= \sum_{\vec{k}}\sum_s |a_s(\vec{k})|^2\langle\vec{K}_f|\vec{k}\rangle_p\langle\vec{k}|\delta(E(\vec{K}_f) - E(s))\,. \end{aligned} \tag{18}$$

Using (7) to eliminate $|a_s(\vec{k})|^2$ and performing the summation over $\vec{k}$, we find that

$$\langle s|_{\text{coh}} \cong \langle \vec{k}_f | e^{-z\alpha_{ep}(\vec{k}_f)} , \tag{19}$$

where $\langle \vec{k}_f|$ is the final state inside of the solid contributing to the spectrum when perfect order exists and

$$\alpha_{ep}(\vec{k}_f) = \frac{\pi \langle \Delta V^2 \rangle \rho(E(\vec{k}_f))}{\left.\dfrac{\partial E(\vec{k})}{\partial k_\perp}\right|_{\vec{k}=\vec{k}_f}} . \tag{20}$$

The coordinate z is taken to be the distance inside of the solid perpendicular to the surface. We are presently neglecting electron-electron scattering, which we shall introduce shortly.

We note that, when the energy dispersion of the final state is given by that of a plane wave, Eq. (20) yields the familiar form[26]

$$\alpha_{ep} = 1/l_{ep}\cos\theta , \tag{21}$$

where

$$\frac{1}{l_{ep}} = \frac{\pi m \langle \Delta V^2 \rangle \rho(E(\vec{k}_f))}{\hbar^2 k_f} \tag{22}$$

and l_{ep} is the mean free path that the electron travels before scattering with a phonon.

This result [Eq. (19)] tells us that the coherent part of the final-state wave function looks much like the wave function that contributes in the perfect crystal, but it decays into the solid at a rate determined by the magnitude of the electron-phonon interaction. However, the charge density of the final state inside of the solid must be the same as that near the surface. As the coherent part of the wave function disappears with increasing z, an incoherent part must increase to preserve the electronic charge density; thus the form of the total final state inside of the solid must be

$$\langle s_f| = \langle s_f|_{\text{coh}} + \langle s_f|_{\text{inc}} , \tag{23}$$

where

$$\langle s_f|_{\text{inc}} = (1 - e^{-2\alpha_{ep}(\vec{k}_f) z})^{1/2} \times \sum_s \sum_{\vec{k}} \bar{a}_s(\vec{k}) \langle \vec{k}| \delta(E(\vec{k}_f) - E(s)) , \tag{24}$$

where $\bar{a}_s(\vec{k})$ is a random variable having the same distribution as $a_s(\vec{k})$ but normalized so that the sum in Eq. (24) corresponds to a unit charge density. The above form of the final state has the property that near the surface it behaves as the final state of the perfect crystal, while far inside of the solid it consists of states distributed throughout the Brillouin zone.

At this point it is convenient to introduce the electron-electron collision processes. Assuming that the electron-electron collisions are incoherent with respect to the electron-phonon collisions, we suggest that they can be taken into account by multiplying $|s_f\rangle$ by the usual electron-electron attenuation factor[26] so that

$$\begin{aligned} \langle S_f| &= \langle s_f| e^{-\alpha_{ee}(\vec{k}_f) z} \\ &= \langle \vec{k}_f | e^{-\alpha(\vec{k}_f) z} + \sum_{\vec{k}} \sum_s \bar{a}_s(\vec{k}) \langle \vec{k}| \\ &\quad \times (1 - e^{-2\alpha_{ep}(\vec{k}_f) z})^{1/2} e^{-\alpha_{ee}(\vec{k}_f) z} \\ &\quad \times \delta(E(\vec{k}_f) - E(s)) , \end{aligned} \tag{25}$$

where

$$\alpha(\vec{k}_f) = \alpha_{ee}(\vec{k}_f) + \alpha_{ep}(\vec{k}_f) , \tag{26}$$

$$\alpha_{ee}(\vec{k}_f) = \frac{\pi |V_{ee}(\vec{k}_f)|^2 \rho(E(\vec{k}_f))}{\left.\dfrac{\partial E(\vec{k})}{\partial k_\perp}\right|_{\vec{k}=\vec{k}_f}} , \tag{27}$$

and $V_{ee}(\vec{k}_f)$ is the screened electron-electron interaction. The above form for the wave function is consistent with an effective mean free path l, of the photoelectron given by

$$\frac{1}{l} = \frac{1}{l_{ee}} + \frac{1}{l_{ep}} , \tag{28}$$

where l_{ee} and l_{ep} are the mean free paths for electron-electron and electron-phonon collisions, respectively. The wave function (25) no longer conserves charge; the missing amplitude has been scattered inelastically by the Coulomb interaction and appears in the detector at much-reduced energy (if at all).

The photoemission intensity from the coherent and incoherent parts do not interfere when averaged over the ensemble, and thus the total intensity can be written as the sum from each part, or

$$I(\vec{k}_f, \vec{\epsilon}, \hbar\omega) = I_{\text{coh}}(\vec{k}_f, \vec{\epsilon}, \hbar\omega) + I_{\text{inc}}(\vec{k}_f, \vec{\epsilon}, \hbar\omega) , \tag{29}$$

where

$$I_{\text{coh}}(\vec{k}_f, \vec{\epsilon}, \hbar\omega) = \sum_{\vec{k}_i} |\langle \vec{k}_f | e^{-z\alpha} \vec{p} \cdot \vec{\epsilon} | \vec{k}_i \rangle|^2 \times \delta(E(\vec{k}_f) - E(\vec{k}_i) - \hbar\omega) , \tag{30}$$

$$\begin{aligned} I_{\text{inc}}(\vec{k}_f, \vec{\epsilon}, \hbar\omega) = \sum_{\vec{k}} \sum_{\vec{k}_i} & |\langle \vec{k}| g(z) \vec{p} \cdot \vec{\epsilon} | \vec{k}_i \rangle|^2 \\ & \times \Delta(E(\vec{k}_f) - E(\vec{k})) \\ & \times \delta(E(\vec{k}_f) - E(\vec{k}_i) - \hbar\omega) \\ & \times \left(\sum_{\vec{k}'} \Delta(E(\vec{k}_f) - E(\vec{k}')) \right)^{-1} , \end{aligned} \tag{31}$$

where

$$g(z) = (e^{2z\alpha_{ep}(\vec{k}_f)} - 1)^{1/2} e^{-z\alpha(\vec{k}_f)} . \tag{32}$$

The square of $g(z)$ is the classical probability that an electron originating from a depth z from the surface scatters with at least one phonon before reaching the surface. The inverse summation in Eq. (31) guarantees that the incoherent intensity has the correct normalization relative to the coherent intensity.

The matrix element in the coherent intensity projects out only initial states that have the same component of momentum parallel to the surface as $\vec{k}_f$, and thus the coherent intensity is expected to exhibit a strong angular dependence. Unlike the coherent intensity, the incoherent intensity includes a sum over all final states having energy $E(\vec{k}_f)$, and, therefore, it is somewhat insensitive to the angle of emission.

The component of momentum parallel to the surface for each of the transitions in the incoherent intensity is conserved, but this component of momentum differs from that of the final state outside, into which the photoelectron escapes. The factors in the matrix elements in Eqs. (30) and (31) that depend upon z result in a relaxation of the component of momentum perpendicular to the surface in the photoionization step. As the temperature increases, $\alpha_{ep}(\vec{k})$ increases, further relaxing the constraints on the momentum conservation perpendicular to the surface and tending to make the coherent spectra resemble one-dimensional densities of states.

The relaxation of momentum conservation perpendicular to the surface for the incoherent intensity is somewhat different from that given for the coherent intensity. The incoherent intensity appears to be very similar to the angle-averaged coherent intensity. The primary difference, however, is that the summation includes optical transitions that normally are outside of the usual escape cone.[27] Spectra obtained at low photon energies, where the influence of the escape cone is important in limiting the transitions that contribute, should exhibit the most dramatic changes with temperature due to this mechanism. Since the escape cone is not important for these transitions, the incoherent spectra from a single-crystal surface should resemble the spectra obtained for polycrystalline films.

Since l_{ee} is usually shorter than l_{ep}, the square root in $g(z)$ can be approximated by the lowest-order term, which corresponds to photoelectrons that have undergone only a single electron-phonon collision. When the final states are approximated as unmixed augmented plane waves, the matrix elements for the coherent and incoherent terms are[1]

$$|\langle\vec{k}_f|e^{-\alpha z}\vec{p}\cdot\vec{\epsilon}\,|\vec{k}_i\rangle|^2 = \frac{\sigma(\vec{k}_f,\vec{k}_i,\vec{\epsilon})}{(\vec{k}_f-\vec{k}_i)_\perp^2+\alpha^2}\,\delta(\vec{k}_{f\parallel}-\vec{k}_{i\parallel}), \tag{33}$$

$$|\langle\vec{k}_f|g(z)\vec{p}\cdot\vec{\epsilon}\,|\vec{k}_i\rangle|^2 \cong \tfrac{1}{4}\pi\alpha_{ep}\frac{\sigma(\vec{k}_f,\vec{k}_i,\vec{\epsilon})}{[(\vec{k}_f-\vec{k}_i)_\perp^2+\alpha^2]^{3/2}} \times\delta(\vec{k}_{f\parallel}-\vec{k}_{i\parallel})\,. \tag{34}$$

As discussed in paper I of this series,[1] the coherent intensity has the form,

$$I_{\text{coh}}(\vec{k}_f,\vec{\epsilon},\hbar\omega)=\sum_n\int\frac{\sigma_n(\vec{k}_f,\vec{k}_i,\vec{\epsilon})\,dk_{i\perp}}{(\vec{k}_f-\vec{k}_i)_\perp^2+\alpha^2} \times\delta(E(\vec{k}_f)-E_n(\vec{k}_i)-\hbar\omega), \tag{35}$$

where

$$\vec{k}_i=\vec{k}_{f\parallel}+\vec{k}_\perp, \tag{36}$$

$$k_{f\parallel}=[(2mE)^{1/2}/\hbar]\cos\theta_v\,, \tag{37}$$

n is the band index which we reintroduce to be consistent with the formalism introduced in paper I of this series, θ_v is the polar angle of emission in the vacuum, and $\sigma_n(\vec{k}_f,\vec{k}_i,\vec{\epsilon})$ is the atomic photoionization cross section of the orbital comprising the initial state. The incoherent intensity has the form

$$I_{\text{inc}}(\vec{k}_f,\vec{\epsilon},\hbar\omega)=\tfrac{1}{4}\pi\sum_n\int d^3k'\int dk_{i\perp}\alpha_{ep}(\vec{k}')\frac{\sigma_n(\vec{k}',\vec{k}_i,\vec{\epsilon})}{[(\vec{k}'-\vec{k}_i)_\perp^2+\alpha^2]^{3/2}}\,\delta(E(\vec{k}_f)-E_n(\vec{k}_i)-\hbar\omega)\,\delta(E(\vec{k}_f)-E(\vec{k}')) \times\Bigl(\sum_{\vec{k}''}\delta(E(\vec{k}_f)-E(\vec{k}''))\Bigr)^{-1}. \tag{38}$$

The form of the incoherent intensity as written in Eq. (38) is valid only when the photoelectrons experience single-phonon collisions, and therefore it does not yield the total incoherent intensity. The relative contributions of the coherent and incoherent intensities can be estimated from elementary considerations. The total coherent intensity, electrons emitted without suffering electron-electron or electron-phonon collisions, is proportional to

$$I_{\mathrm{coh}}(\vec{\mathrm{k}}_f, \vec{\epsilon}, \hbar\omega) \propto l = \frac{l_{ee} l_{ep}}{l_{ee} + l_{ep}} . \tag{39}$$

The total coherent and incoherent intensities, i.e., electrons emitted without suffering electron-electron collisions, must satisfy

$$I_{\mathrm{coh}}(\vec{\mathrm{k}}_f, \vec{\epsilon}, \hbar\omega) + I_{\mathrm{inc}}(\vec{\mathrm{k}}_f, \vec{\epsilon}, \hbar\omega) \propto l_{ee} . \tag{40}$$

Using Eqs. (39) and (40) we find that

$$I_{\mathrm{inc}}(\vec{\mathrm{k}}_f, \epsilon, \hbar\omega) \propto \frac{l_{ee}^2}{l_{ee} + l_{ep}} \tag{41}$$

and

$$\frac{I_{\mathrm{coh}}(\vec{\mathrm{k}}_f, \vec{\epsilon}, \hbar\omega)}{I_{\mathrm{inc}}(\vec{\mathrm{k}}_f, \vec{\epsilon}, \hbar\omega)} = \frac{l_{ep}}{l_{ee}} . \tag{42}$$

As the temperature increases and l_{ep} decreases, the coherent intensity decreases in strength, while the incoherent intensity increases in strength. This is in contrast to the results found in Sec. IV B, in which the spectra are only broadened and shifted when the interatomic electron-phonon interaction affects only the initial states.

It is necessary for $l_{ep} \sim l_{ee}$ in order that k conservation be significantly relaxed. It is not clear whether this limit is ever achieved in real materials before melting occurs.

The lifetime broadening of the final state either by electron-electron collisions or by electron-phonon collisions does not lead to corresponding energy broadening of the photoelectron spectra taken for a single-photon energy. This occurs since the energy of the final state detected is defined experimentally by the analyzer. The only noticeable effect of the energy broadening of the final state is a breakdown in the coherency of emission from the layers, resulting in a relaxation of the conservation of the component of momentum perpendicular to the surface. (This energy broadening of the final state, however, becomes apparent only when the photoelectron distribution exhibits sharp structure due to the final state.) Thus the changes in the spectra due to the electron-phonon interaction influencing the final state (momentum but no energy broadening) are opposite those caused by this interaction influencing the initial state (energy but no momentum broadening).

V. DISCUSSION

The effects of the intra- and interatomic electron-phonon interaction upon the angle-resolved photoelectron spectra from the bulk bands of solids for the three separate cases given by Eqs. (4), (12), and (29)–(32) are contained in the master formula

$$\begin{aligned} I(\vec{\mathrm{k}}_f, \vec{\epsilon}, \hbar\omega) = {} & \sum_{k_i} |\langle k_f | e^{-z\alpha(\vec{\mathrm{k}}_f)} \vec{\mathrm{p}} \cdot \vec{\epsilon} \,| k_i \rangle_d |^2 \Delta(E(\vec{\mathrm{k}}_f) - E(\vec{\mathrm{k}}_i) - \hbar\omega) \\ & + \sum_{k} \sum_{k_i} |\langle k | g(z) \vec{\mathrm{p}} \cdot \vec{\epsilon} \,| k_i \rangle_d |^2 \Delta(E(\vec{\mathrm{k}}_f) - E(\vec{\mathrm{k}}_i) - \hbar\omega) \times \delta(E(\vec{\mathrm{k}}_f) - E(\vec{\mathrm{k}})) \left[\sum_{\vec{\mathrm{k}}''} \delta(E(\vec{\mathrm{k}}_f) - E(\vec{\mathrm{k}}'')) \right]^{-1} . \end{aligned} \tag{43}$$

The intra-atomic electron-phonon interaction is taken into account by using the distorted basis set to calculate the matrix elements in Eq. (43) between the initial and final states. The effects of the interatomic electron-phonon interation upon the initial states are taken into account by the function $\Delta(E)$, and their effects upon the final state are taken into account by the second term in Eq. (43) and by the exponential factors in the matrix elements. The distorted basis set should also be used to calculate the electron-phonon matrix elements in Eqs. (8) and (9).

The reader must be warned that Eq. (43) does not include any interferences between the three cases discussed and, therefore, it might not be entirely accurate when two or three of them have comparable influence upon the spectra. While Eq. (43) otherwise covers the general case, it is of interest to discuss whether there are situations when one or two of the cases dominate the temperature dependence of the spectra.

In metals the electron-phonon interaction for the free-electron-like final state is never large and, therefore, the first term in Eq. (43) describes the spectra for all photon energies. At low photon energies the intra-atomic effects are unimportant, and the initial-state energy broadening and shifting are the only significant temperature-dependent features observable in the spectra. The effects of temperature should be easily observable in materials in which the intrinsic width due to Auger effects is small, such as free-electron-like metals and noble metals. The large Auger broadening in transition metals[28] should make it difficult to observe the initial-state broadening effects due to lattice vibrations.

The experimental results of Hiemann and Neddermeyer[15] on Au for $h\nu = 16.9$ eV appear to be influenced primarily by the broadening and shifting of the initial-state energies. The weak dependence of a peak they observe near the Fermi energy is probably attributable to the fact that the contributing initial state falls in a region of a low density of states and that it is derived from extended s-like orbitals, which have a small electron-phonon interaction.[12]

The second term in Eq. (43) becomes significant only when $l_{ep} \sim l_{ee}$. This condition is most likely to be satisfied by semiconductors and ionic crystals at low photon energies and high temperatures. Since the Auger widths of such materials are small, both the final-state scattering and the initial-state shifting and broadening should be simultaneously present. In this case not only do the peaks given by the first term in Eq. (43) appear to broaden and shift with increasing temperature, but they also decrease in strength as an angle-averaged component [the second term in Eq. (43)] increases in intensity. The experimental results of Grandke and Cardona[16] on PbS and PbSe appear to be consistent with such a behavior. The angle-averaged spectra of Bauer *et al.*[12] do not strongly exhibit the second term in Eq. (43) since it is so similar to the angle average of the first term. The primary changes in their spectra appear to be due to the energy broadening and shifting of the energies of the initial and final states. In their data the smearing and broadening of the final state is noticeable since the final state introduces structure into the spectra at the low photon energies used.

For all materials at high photon energies and temperatures, where $W(\vec{k}_f, \vec{k}_i) > 1$, the second term in Eq. (43) is small and the spectra must approach the energy-broadened and -shifted density of states given by the first term in Eq. (43), or

$$I(\vec{k}_f, \epsilon, \hbar\omega) = \sum_{\vec{k}_i, n} \sigma_n(\vec{k}_f, \vec{k}_i, \vec{\epsilon}) \times \Delta(E(\vec{k}_f) - E(\vec{k}_i) - \hbar\omega). \tag{44}$$

This limit appears to have been verified experimentally by Williams *et al.*[13]

Comments upon the recent work of Sayers and McFeely[18] are due at this point. As mentioned earlier, a perturbative method, such as used by Sayers and McFeely[18] is unlikely to account for the effects due to the intra-atomic electron-phonon interaction. However, the conclusions they reached, namely, the electron-phonon interaction is unimportant in the XPS regime, is in agreement with the conclusions reached here concerning the scattering of the final state by *interatomic* electron-phonon interactions which is weak enough to be appropriately accounted for by perturbative methods.

The effects of phonons must be considered when one is attempting to determine whether an observed peak is due to a surface or bulk state. Surface states are usually formed close in energy (~0.3 eV) to the edges of bulk bands. Often, disagreement in the observed positions of peaks predicted by band theory for the bulk is taken to be evidence for the existence of surface states.[29] However, since band calculations are made almost exclusively for the perfect lattice, they might not be capable of predicting the position in energy of the observed features from the bulk. Furthermore, since the position in energy of a surface state is sensitive to the surface potential, lattice vibrations might be able to upset the stability of the surface state, causing it to merge completely with the bulk states nearby in energy.

Such mechanisms might be influencing the so-called surface states of the (111) face of the noble metals occurring near the Fermi energy.[30,31] The gap between the lowest free-electron-like bands of the L point is due primarily to the (111) pseudopotential interaction.[32] As discussed by Yu and Cardona,[8] the pseudopotential in the vibrating lattice is weakened by the Debye-Waller factor, which causes the first-order gaps to decrease by the same amount. We estimate that this mechanism causes the L_2' bulk features to be ~0.4 eV higher at room temperature than calculated by the usual band-structure theory. If this were true, the position of the L_2' feature ought to display a strong temperature dependence.

VI. SUMMARY AND CONCLUSIONS

The effects of phonons in modifying the angle-resolved photoemission from the bulk bands of solids has been discussed in terms of intra-atomic and interatomic effects. The temperature dependence of the spectra of photoelectrons obtained at low photon energies from metals ought to reveal directly the size of the electron-phonon interaction throughout the entire Brillouin zone. Such information might provide insights concerning the influence of special features of the band upon the superconducting properties of materials. The temperature dependence of the angle-resolved spectra of semiconductors and ionic crystals is more difficult to interpret, owing to the scattering of the final state by the interatomic electron-phonon interaction. In all materials the intra-atomic electron-phonon interaction guarantees that the angle-resolved spectra at high temperatures and high photon energies approach the density of initial states.

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