PHYSICAL REVIEW B VOLUME 15, NUMBER 10 15 MAY 1977

Emission spectra and phonon relaxation*

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(Received 18 October 1976)

Absorption and emission spectra are calculated for a model which has phonon coupling to a localized electronic state. The lifetimes of the electronic state, and of the phonons, are both included. Thus the emission spectrum is influenced by the amount of relaxation in the phonon system. If the emission is slow, the phonons relax around the excitation, and the emission has a Franck-Condon shift. If the emission is fast, the phonons do not have time to relax, and the shift is considerably reduced.

I. INTRODUCTION

In a solid, the absorption and emission of photons are complementary experiments which provide different information about the system under investigation. If the photon absorption causes the excitation of a localized electron, the emission is not at the same frequency as the absorption, because of phonon and electronic relaxation around the excitation. The outstanding example of this is in the old model for F-center absorption, where the emission and absorption frequencies differ by as much as 2 eV. This difference is called the Franck-Condon shift.[1,2]

The present investigation was stimulated by the large phonon broadening reported for the x-ray absorption edge in metallic lithium.[3-5] Since the core hole is localized, one would naively expect that—like the F center—there would be a significant (i.e., of order 1 eV) shift between the emission and absorption edges. The present experimental situation is unclear, and there may indeed exist an edge shift between emission and absorption of as much as 0.3 eV.[4] The theoretical situation was anticipated by Hedin,[6] who earlier pointed out why the Franck-Condon shift may be reduced or not even occur. If the core hole lives a very short time compared to the time scale of phonons, then the phonon polarization and relaxation do not get enough time to set up around the core hole before the emission takes place. This happens if $\omega_p \tau \ll 1$, where τ is the hole lifetime, and ω_p is a typical phonon frequency.

Another way to describe Hedin's model is to note that the hole has two decay channels: Auger decay and photon emission. Auger decay is usually much more probable, and is the dominant contribution to the lifetime. Thus, the photon emission must occur soon after the absorption step, if it is ever going to happen, otherwise the core hole will decay by Auger process.

Here, we present a mathematical theory to describe this process. One motivation was the experimental report for lithium that the Auger decay width was $\Gamma = 0.04 \pm 0.03$ eV.[5] Since zone-edge LA phonons in Li have[7] $\omega_{\mathrm{LA}} \sim 0.04$ eV then $\omega_{\mathrm{LA}} \sim \Gamma$. Is this large or small? Does relaxation occur or not? Our results show that some relaxation should occur for this value of damping constant, so that some Franck-Condon shift should be observed. Furthermore, the emission line shape should not be very symmetric. Our calculated absorption spectra are little changed by variations in these parameters.

Our method of calculation follows that of Almbladh.[8] He was concerned with the incomplete relaxation of plasmons, and their influence on Auger decay. He treated plasmons as bosons, and used a Fröhlich Hamiltonian for the hole-plasmon coupling. We shall do the same for phonons, so the formal mathematics is identical. The main difference in our results is that we include finite-temperature effects. Almbladh could safely use a zero-temperature result for plasmons which have $\hbar\omega_p \gg K_B T$ for room temperatures. Temperature effects are important for phonons, so we needed to derive the finite-temperature equivalent of his result. Our numerical results span a different parameter range than his, reflecting the difference between the plasmon and phonon energies, since he never has $\omega_p \tau < 1$. There are also some minor differences in the method we use to introduce damping and dispersion. Some related work was also done by Yue and Doniach,[9] who investigated the effect of electronic relaxation on the lithium spectra.

McMullen and Bergersen[10] also reported a related calculation of lifetime effects on emission. They assumed core-hold excitation by electron bombardment, as did Almbladh,[8] but used a different mathematical technique for introducing it. Consequently, the answers come out mathematically different.

The calculations of the next sections actually pertain to the F-center case of localized emission and absorption. Thus, we calculate peaks for emission and absorption. This is slightly easier than the edge emission case. However, the two are simply related, since the derivative of the edge shape gives the F-center peaks.

II. WITHOUT PHONONS

We will consider a two-step optical process. In the first step, the absorption of a photon takes an electron from a localized state to an excited state. In the second step, the emission of a second photon returns an electron to the same initial state. This is a type of two-step process, wherein the intermediate state has an electron excited. We assume that the initial electron came from a filled electronic shell, so that its excitation created a hole in the intermediate state.

The hole is actually excited—not virtually excited—and exists for a mean lifetime τ. This lifetime is given by the rate of Auger τ_0 and photon emission w_2 rates

$$1/\tau = 1/\tau_0 + w_2 .$$

If w_1 is the rate of absorption of the initial photon, and N_q, $N_{q'}$, and N_h are the densities of initial photons, final photons, and holes, then we can write down the usual rate equations for the: rate of absorption,

$$\frac{\partial N_q}{\partial t} = -w_1 N_q ;$$

rate of emission,

$$\frac{\partial}{\partial t} N_{q'} = w_2 N_h ;$$

and hole population,

$$\frac{\partial}{\partial t} N_h = w_1 N_q - \frac{N_h}{\tau} .$$

Now, in equilibrium we get

$$N_h = \tau w_1 N_q ,$$

so that the net rate of photon emission w is simply

$$w = w_1 w_2 \tau . \tag{1}$$

This is easy to interpret as the product of two factors: w_1 is the rate of absorption, while

$$\tau w_2 = \frac{w_2}{1/\tau_0 + w_2}$$

is the fraction of those absorbed which decay by x-ray emission.

Next we wish to rederive (1) using the second-order golden rule of quantum mechanics. The two-step process is shown in Fig. 1. A photon of frequency ω_1 makes an electron-hole pair in states p and h, respectively. The hole h decays by recombining with an electron in state k with photon emission of frequency ω_2. It could be, but is not essential, that p and k are the same electron. Thus there is an interaction Hamiltonian

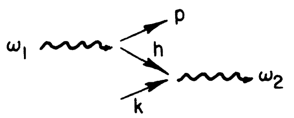

FIG. 1. Two-step optical process under consideration. The photon ω_1 creates an electron p and hole h. The hole propagates until it meets another electron k, when it recombines to create another photon ω_2.

$$V(t) = V_1(t) + V_2(t) + hc ,$$
$$V_1(t) = M_1 a_1 d^\dagger C_p^\dagger \exp(-i\Omega_1 t) ,$$
$$V_2(t) = M_2 a_2^\dagger d C_k \exp(i\Omega_2 t) ,$$
$$\Omega_1 = \omega_1 - \xi_p - \xi_h ,$$
$$\Omega_2 = \omega_2 - \xi_k - \xi_h ,$$

where a, C, and d are photon, electron, and hole operators. The second-order golden rule given for the amplitude of emission after time t to be

$$S^{(2)}(t) = (-i)^2 \int_0^t dt_1 \int_0^t dt_2\, V_2(t_1) \times V_1(t_2)\,|\,\text{initial state}\rangle . \tag{2}$$

The time ordering above was chosen to reflect our assumption that holes cannot exist initially, so that V_1 must be to the right of V_2. The emission amplitude above is correct if the hole cannot decay by other means. But if it can decay by Auger or other means, then this feature must be added to the rate process. We do this by inserting the factor $\exp[-\gamma(t_1 - t_2)]$ into the integrand

$$S^{(2)}(t) = (-i)^2 M_1 M_2 \int_0^t dt_1 \int_0^{t_1} dt_2 \times e^{-\gamma(t_1-t_2)} e^{i\Omega_2 t_1} e^{-i\Omega_1 t_2} .$$

This arises from the factor

$$d(t_1)\, d^\dagger(t_2)\,|\,\text{initial state}\rangle .$$

Thus, a hole is destroyed at t_1, if created at t_2, with a decaying probability $\exp[-\gamma(t_1 - t_2)]$. The time integrals can all be done

$$S^{(2)} = M_1 M_2 \left(\frac{e^{it(\Omega_2-\Omega_1)} - 1}{(\Omega_2 - \Omega_1)(\Omega_1 + i\gamma)} - \frac{e^{it(\Omega_2+i\gamma)} - 1}{(\Omega_1 + i\gamma)(\Omega_2 + i\gamma)} \right) .$$

The transition rate is found by squaring, taking the derivative with time, and then the infinite time limit. Only the first term contributes, with the result that the emission rate is

$$w = \frac{2\pi}{\hbar} \sum_{hp} M_1^2 M_2^2 \frac{\delta(\Omega_1 - \Omega_2)}{\Omega_1^2 + \gamma^2} . \tag{3}$$

If we identify the rate of absorption as

$$w_1 = \sum_p M_1^2 \frac{2\gamma}{\Omega_1^2 + \gamma^2} ,$$

and the rate of emission as

$$w_2 = \frac{2\pi}{\hbar} \sum_k M_2^2 \delta(\Omega_1 - \Omega_2) ,$$

then (3) becomes

$$w = w_1 w_2 / 2\gamma .$$

Finally, if we identify the relaxation time $\tau = (2\gamma)^{-1}$, then this expression is the same as (1). Thus, we have a quantum-mechanical derivation of this simple rate formula. Next, we must put phonons into this two-step process.

III. UNDAMPED PHONONS

Phonon processes are now introduced into the transition rate. The hole state is assumed to have a linear coupling to phonons

$$H_p = d^\dagger d M_0 (b + b^\dagger) + \omega_0 b^\dagger b .$$

The phonon coupling affects the line shape of both emission and absorption.

The line shapes in absorption were first calculated by Lax,[11] and Huang and Rhys,[12] many years ago. A general mathematical formalism was developed by Feynman,[13] and has been used in a number of contexts.[14-17] We now wish to consider multistep transitions. To calculate emission we need to do two steps. In order to keep the notation simple, we consider just a single phonon mode of frequency ω_0. The sum over all phonon modes is simple to include at the end.

Our model Hamiltonian is

$$H = \xi_n d^\dagger d + \sum_p \xi_p C_p^\dagger C_p + \sum_\lambda \omega_\lambda a_\lambda^\dagger a_\lambda + V + H_p ,$$

where V and H_p have been given above. We do the standard canonical transformation

$$H' = e^s H e^{-s} = (\xi_n - \Sigma_0) d^\dagger d + \sum_p \xi_p C_p^\dagger C_p$$

$$+ \sum_\lambda \omega_\lambda a_\lambda^\dagger a_\lambda + V' + \omega_0 b^\dagger b ,$$

$$S = (M_0/\omega_0) d^\dagger d (b^\dagger - b) ,$$

$$V_1'(t) = M_1 d^\dagger a_1 C_p^\dagger X^\dagger(t) e^{-i\Omega_1' t} ,$$

$$V_2'(t) = M_2 d a_2^\dagger C_k X(t) e^{i\Omega_2' t} ,$$

$$\Omega_{1,2}' = \Omega_{1,2} + \Sigma_0, \quad \Sigma_0 = M_0^2/\omega_0 ,$$

$$X(t) = \exp[(M_0/\omega_0)(b^\dagger e^{i\omega_0 t} - b e^{-i\omega_0 t})] .$$

The factors $X(t)$ give the phonon distortion about the hole. Thus, the amplitude of photon emission is now

$$S^{(2)} = -M_1 M_2 \int_0^t dt_1 \int_0^{t_1} dt_2 e^{-\gamma(t_1 - t_2)} \times e^{i\Omega_2' t_1 - i\Omega_1' t_2} X(t_2) X^\dagger(t_1) .$$

The intensity of emission is

$$|S^{(2)}|^2 = M_1^2 M_2^2 \int_0^t dt_3 \int_0^{t_3} dt_4 e^{-\gamma(t_3 - t_4)} e^{-it_3 \Omega_2'} e^{it_4 \Omega_1'} \int_0^t dt_1 \int_0^{t_1} dt_2 e^{-\gamma(t_1 - t_2)} e^{i\Omega_2' t_1} e^{-i\Omega_1' t_2} \langle X(t_4) X^\dagger(t_3) X(t_1) X^\dagger(t_2) \rangle \tag{4}$$

The bracket $\langle\ \rangle$ means to average this quantity over the thermal distribution of phonons in the system. This result is the direct extension to a two step process of the Lax-Feynman result for a single step.[11,13] The general prescription for evaluating these multi-$X(t)$ averages is given in the Appendix. There, it is shown that the above is

$$\langle X(t_4) X^\dagger(t_3) X(t_1) X^\dagger(t_2) \rangle = \exp\{-(M_0^2/\omega_0^2)[(N+1)(2 - e^{-i\omega_0(t_1 - t_2)} + e^{-i\omega_0(t_3 - t_2)} - e^{-i\omega_0(t_4 - t_2)}$$
$$- e^{-i\omega_0(t_3 - t_1)} + e^{-i\omega_0(t_4 - t_1)} - e^{-i\omega_0(t_4 - t_3)}) + N(\ \ )^*]\} .$$

The notation $(\ \ )^*$, which we will use throughout, means that the factor multiplying N is the complex conjugate of that multiplying $N+1$. N is the thermal occupation number of phonons.

The transition rate is again obtained by differentiating by time, and taking the infinite time limit. The time t appears twice in (4). So its derivative yields two terms, which are complex conjugates of each other

$$w(\Omega_1, \Omega_2) = \lim_{t \to \infty} \frac{\partial}{\partial t} |S^{(2)}|^2 = 2 \,\mathrm{Re} \int_0^t dt_4 \int_0^t dt_1 \int_0^{t_1} dt_2 f(t_1, t_2, t_3 = t, t_4) ,$$

where f is the integrand of (4). Next we change integration variables to

$$\tau_2 = t_1 - t_2 , \quad \tau_4 = t - t_4 , \quad \tau_1 = t - t_1 ,$$

with the result

$$w(\Omega_1,\Omega_2)=2M_1^2M_2^2\,\mathrm{Re}\int_0^\infty d\tau_1 e^{i\Omega_{12}\tau_1}\int_0^\infty d\tau_2 e^{-\tau_2(\gamma-i\Omega_1')}\int_0^\infty d\tau_4 e^{-\tau_4(\gamma+i\Omega_1')}$$

$$\times\exp-\frac{M_0^2}{\omega_0^2}\{(N+1)[2-e^{-i\omega_0\tau_2}-e^{i\omega_0\tau_4}-e^{-i\omega_0\tau_1}(1-e^{-i\omega_0\tau_2})(1-e^{i\omega_0\tau_4})]+N(\quad)^*\}\,. \tag{5}$$

This is our basic result. It is a bit unwieldy, so we have not tried to evaluate it. It gives the emission spectra $w(\Omega_1,\Omega_2)$ as a function of the excitation frequency Ω_1.

The absorption spectra $\alpha(\Omega_1)$ can be calculated from this result by integrating over all emission events

$$\alpha(\Omega_1)=\int_{-\infty}^{\infty}d\,\frac{\Omega_2}{2\pi}\,w(\Omega_1,\Omega_2)\,.$$

This integration creates the delta function $\delta(\tau_1)$ which eliminates the integral over τ_1,

$$\alpha(\Omega_1)=2M_1^2M_2^2\,\mathrm{Re}\int_0^\infty d\tau_2 e^{-\tau_2(\gamma-i\Omega_1')}\int_0^\infty d\tau_4 e^{-\tau_4(\gamma+i\Omega_1')}\exp-\frac{M_0^2}{\omega_0^2}[(N+1)(1-e^{-i\omega_0(\tau_2-\tau_4)})+N(\quad)^*]\,.$$

After a change of integration variables $t=\tau_2-\tau_4$, this can be written

$$\alpha(\Omega_1)=4\tau\,\mathrm{Re}\int_0^\infty dt\,e^{i\Omega_1 t}\,e^{-\gamma t}\,e^{-\phi(t)}\,, \tag{6}$$

$$\phi(t)=(M_0^2/\omega_0^2)[(2N+1)(1-\cos\omega_0 t)-i(\omega_0 t-\sin\omega_0 t)]\,, \tag{7}$$

where the self-energy term Σ_0 has been included in $\phi(t)$. This is the standard result that the absorption is affected by phonons, $\phi(t)$, and by the Auger width $\exp(-\gamma t)$. Current practice seems to be to change this to frequency integrals, after which each factor is included by successive convolutions. But it seems much more economical to express the result as above, wherein each factor is separate in time.

In order to evaluate the emission from (5), it is necessary to assume some value for the absorption frequency. Instead, we tried an alternate procedure of assuming that the absorption was done by a white light—i.e., a uniform distribution of absorption frequencies:

$$E(\Omega_2)=\int_{-\infty}^{\infty}\frac{d\Omega_1}{2\pi}\,w(\Omega_1,\Omega_2)\,.$$

This is the quantity which we evaluated. Doing this integral creates in (5) a delta function $\delta(\tau_1+\tau_2-\tau_4)$ which we use to eliminate the τ_4 integration. The resulting time integrals can be arranged into the form

$$E(\Omega_2)=2\,\mathrm{Re}\int_0^\infty d\tau_1 I(\tau_1)\exp[-i\tau_1(\Omega_2+2\Sigma_0)-\gamma\tau_1-\phi(\tau_1)]\,, \tag{8}$$

$$I(\tau_1)=\int_0^\infty d\tau_2 e^{-2\gamma\tau_2}\exp\left(-2i\frac{M_0^2}{\omega_0^2}[\sin(\omega_0\tau_2)-\sin\omega_0(\tau_1+\tau_2)]\right)\,. \tag{9}$$

This was evaluated directly on the computer, as a double integral in time. For small γ they converge slowly. This was overcome by using the fact that the integrand is mostly periodic in time, with period $2\pi/\omega_0$. For example, the integral $I(\tau_1)$ can be written

$$I(\tau_1)=\sum_{n=0}^{\infty}\int_{2\pi n/\omega_0}^{2\pi(n+1)/\omega_0}d\tau_2 e^{-2\gamma\tau_2}g(\tau_2)$$

$$=(1-e^{-4\pi\gamma/\omega_0})^{-1}\int_0^{2\pi/\omega_0}d\tau_2 e^{-2\gamma\tau_2}g(\tau_2)\,,$$

where $g(\tau_2)$ is everything else in the integrand, and is periodic. The summation over n reduces the computation to a finite integral. The same procedure works for the other time integral.

The result (8) appears to have a sensible form. The frequency factor $\Omega_2+2\Sigma_0$ shows that the emission should peak at $\Omega_2\sim-2\Sigma_0$, which is correct since this is the well-known Franck-Condon shift between emission and absorption. The additional factors $\exp(-\gamma\tau_1)$ and $\exp[-\phi(\tau_1)]$ are the Auger and phonon contributions to the emission line shape. Thus, our main new result is the factor $I(\tau_1)$ which evidently includes the effect on the emission spectra of the absorption process.

Some typical numerical results are shown in Fig. 2 for several values of the Auger width γ. The other parameters were chosen in an attempt to fit the K-shell x-ray edge of metallic lithium. Lithium does not have optical phonons, so we used the value estimated for LA phonons at the zone edge, $\omega_{\mathrm{LA}}\sim0.045$ eV for which there is a peak in the phonon density of states.[7] From the large phonon broadening $\Gamma_{\mathrm{ph}}=0.26$ eV, we estimated $M_0^2/\omega_0^2=6$. At room temperature we get $N=0.21$. These are the phonon parameters used to calculate the figures. Several other parameter sets were also computed, and they showed the same type of physical phenomena.

In Fig. 2(a), the solid line is the absorption spectra calculated from (6) and (7). Its width is dominated by phonons. In fact, the width is about six phonon energies, which gives the value 0.26 eV which was used to fit the parameters. Only one absorption spectra is shown, but it changes little over the increasing range of Auger parameters.

For both emission and absorption, the line shape for small γ is actually a sum of sharp Lorentzians, spaced one phonon energy apart. We actually plot just the peak height of the Lorentzian, through which we draw a smooth envelope.

The emission spectra in Fig. 2(a) is shown for very small values of Auger line width $\gamma = 0.0025$ eV. This means the excited state lives a long time. The spectra is very surprising, and is double humped! One might have expected the emission to have a single peak at the Franck-Condon shifted value of $\Omega_2 = -2\Sigma_0 = -12\,\omega_0$. Instead, there are two equal peaks at $-4\Sigma_0 \sim -24\,\omega_0$, and 0. There is a minimum at the value $\Omega_2 \sim -2\Sigma_0$. This behavior occurs because there is no damping of phonons in the theory. So when phonons are made during the absorption, they continue to oscillate, and affect the emission. Figure 3 is a configurational coordinate model of this process.[1,2] The absorption of the photon makes the phonon system at point A. The phonons continue to oscillate between points A and C. The point C is the emission point which gives the second hump at $\Omega_2 \sim -4\Sigma_0 \sim -24\,\omega_0$. If the phonon system were to relax, then the emission would be from the point B. However, there is no phonon relaxation in the model yet, so A and C are the points of maximum emission. The point B is an emission minimum because the excited state does not spend much time there during its oscillation.

Figure 2(b) shows the behavior of the emission when the Auger lifetime is decreased, by increasing the value of γ. The low-frequency maximum, corresponding to the emission transition C, decreases compared to the emission from A. At the value of $\gamma = 0.05$ eV, this peak has vanished, and the emission is single peak. Here, the excited state is short lived, so that the phonon system does not get time to adjust to the presence of the excited state. Hence, for short lifetimes, the Franck-Condon shift indeed disappears. The calculations show that the value of $\gamma \simeq \omega_0$ is sufficient. This value is still small enough that the absorption spectra is nearly unchanged from that in Fig. 2(a). Another feature of this result is that the emission and absorption do not coincide, but that there is a small shift of $-2\omega_0 \sim 0.1$ eV between them. This small shift persists even if the value

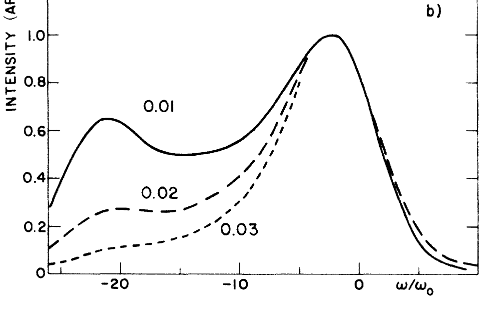

FIG. 2. (a) Absorption (solid line) and emission (dashed line) for the case of small Auger damping or long-lived hole state. The absorption shows the effects of phonon broadening. The emission shows two peaks due to the ringing in the excited state. (b) Successive emission peaks as the Auger damping is increased with values 0.01, 0.02, and 0.03 eV. All curves arbitrarily normalized to unit peak height.

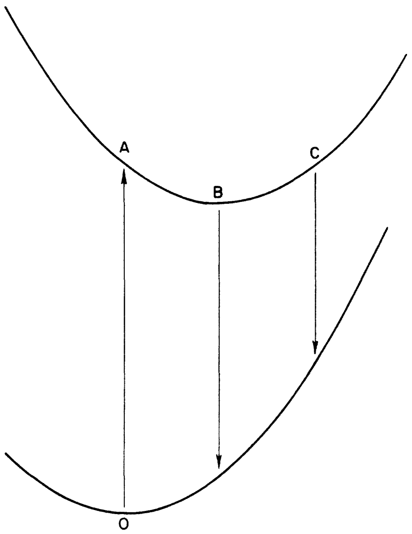

FIG. 3. Configurational coordinate representation of our process. The parabolic curves represent phonon-energy distortions in the ground (lower) and excited (upper) electronic states. The absorption is the arrow A. With phonon damping, the excited state phonons would relax to B, and emission here produces the usual Franck-Condon shift. Without phonon damping, the excited state oscillates between points A and C. The two-humped emission spectra of Fig. 2(a) arises from emissions from A and C.

of γ is raised further.

Our objective has been to produce a theory which, as depicted in Fig. 3, describes the absorption process A and the emission process B. Obviously, it is necessary to include damping or relaxation of the phonon system. This will eliminate the ringing between points A and C. This is done next.

IV. PHONON DAMPING

Our numerical integrals (6) for absorption and (8) for emission are just Fourier transforms. As such, they may either be negative or positive. However, as causal functions, they must be positive or the theory is in error. This remark is appropriate because our first attempts to include phonon damping produced spectra which had negative regions. These early attempts were obviously acausal. Determining the proper method of including phonon damping is a subtle process.

A very reasonable method has been proposed by Langreth.[18] His suggestion was intended for treating electronic excitations. However, the idea may also be applied to phonons or any other type of excitation. The phonon damping causes the system to no longer respond at a single frequency ω_0, but instead to have a distribution of frequencies. This is described by a spectral distribution function, which we take to have the form

$$A(\omega)=B/[(\omega^2-\omega_0^2)^2+4\omega_0^2\Delta^2], \tag{10a}$$

where B is a normalization constant

$$B=4\omega_0\Delta\sqrt{2}(\omega_0^4+4\omega_0^2\Delta^2)^{1/2}[(\omega_0^4+4\omega_0^2\Delta^2)^{1/4}+\omega_0^2]^{-1/2} \tag{10b}$$

determined by the condition

$$1=\int_0^\infty \frac{d\omega}{2\pi}A(\omega).$$

Langreth simply suggested that $\phi(\tau)$ be given by

$$\phi(\tau)=\int_0^\infty \frac{d\omega}{2\pi}\frac{M_0^2(\omega)}{\omega^2}A(\omega)\times\{[N(\omega)+1](1-e^{-i\omega t}-i\omega t)+N(\ \ )^*\}, \tag{11}$$

where we have summed over all frequencies, weighted by the spectral distribution function. We have adopted this procedure, and extended it to all phonon functions in the integrand—$I(\tau_1)$ in (9) now has the exponent

$$-2i\int_0^\infty \frac{d\omega}{2\pi}A(\omega)\frac{M_0^2(\omega)}{\omega^2}[\sin(\omega\tau_2)-\sin\omega(\tau_1+\tau_2)]. \tag{12}$$

This is the result for a single phonon state.

Almbladh[8] also noticed that the system would oscillate indefinitely unless some method was introduced to stop it. He used the dispersion of the plasmons. If a mode has dispersion, it will move away from the excitation center, and no longer cause ringing. Thus damping and dispersion have a similar effect upon the spectra. They also have a similar mathematical form. To put in dispersion, we generalize the result to include all phonons of different q and polarization λ. One gets the same exponential factor for each mode, so the exponential factors are summed over modes:

$$\phi(t)=\sum_{q,\lambda}\frac{M_{q\lambda}^2}{\omega_{q\lambda}^2}\{(2N_{q\lambda}+1)[1-\cos(t\omega_{q\lambda})]-i[t\omega_{q\lambda}-\sin(t\delta_{q\lambda})]\},$$

$$\Sigma_0=\sum_{q\lambda}\frac{M_{q\lambda}^2}{\omega_{q\lambda}},$$

and the exponent in (9) is

$$-2i\sum_{q\lambda}\frac{M_{q\lambda}^2}{\omega_{q\lambda}^2}[\sin(\tau_2\omega_{q\lambda})-\sin\omega_{q\lambda}(\tau_1+\tau_2)].$$

The sum over phonons is done by defining an effective interaction function

$$F(\omega)=2\pi\sum_{q\lambda}M_{q\lambda}^2\,\delta(\omega-\omega_{q\lambda}),$$

$$\phi(t)=\int_0^\infty\frac{d\omega}{2\pi}\frac{F(\omega)}{\omega^2}\times\{[N(\omega)+1](1-e^{-i\omega t}-i\omega t)+N(\ \ )^*\}, \tag{13}$$

by comparing (13) and (11), one can see that $F(\omega)$ plays a role similar to $M_0^2A(\omega)$. If there is no dispersion, $F(\omega)$ is a delta function while band dispersion gives a width to $F(\omega)$. Similarly, if one wished to use both dispersion and damping, then $F(\omega)$ has the form

$$F(\omega)=2\pi\sum_{q\lambda}M_{q\lambda}^2A(q,\omega),$$

where $A(q,\omega)$ is the spectral function of q and ω. Thus, dispersion and damping play a similar role in affecting the relaxation around the excitation center.

Our computations will use the form of $\phi(\tau)$ given in (11) with (10a) for $A(\omega)$. This width can either be interpreted as a phonon bandwidth, or damping, or a combination of both.

For our calculations, we used (11) and (12). A deformation potential coupling was assumed $M_0^2(\omega)=C\omega$, where C is a constant. It is also convenient to introduce a renormalized frequency $\tilde{\omega}$ and damping constant Γ by the relations

$$\omega_0^2=\tilde{\omega}^2-\Gamma^2,\quad \omega_0\Delta=\tilde{\omega}\Gamma,$$

which may be solved to give

$$\tilde{\omega}^2 = \tfrac{1}{2}\left[(\omega_0^4 + 4\omega_0^2\Delta^2)^{1/2} + \omega_0^2\right],$$

$$\Gamma^2 = \tfrac{1}{2}\left[(\omega_0^4 + 4\omega_0^2\Delta^2)^{1/2} - \omega_0^2\right].$$

This is convenient because $A(\omega)$ has poles at the points $\pm(\tilde{\omega} \pm i\Gamma)$ and B in (10) is simplified to

$$B = 4\Gamma(\tilde{\omega}^2 + \Gamma^2).$$

The integral in (12) and part of (11) may be done by contour integral. We define

$$\phi_s(t) = \frac{C}{2\pi}\int_0^\infty \frac{d\omega}{\omega} A(\omega)\sin(\omega t),$$

which is evaluated to be

$$\phi_s(t) = \frac{C}{\tilde{\omega}}\left\{ e^{-\Gamma t}\left[\left(\frac{\tilde{\omega}^2 - \Gamma^2}{\tilde{\omega}^2 + \Gamma^2}\right)\sin(\tilde{\omega}t) - \frac{2\Gamma\tilde{\omega}}{\tilde{\omega}^2 + \Gamma^2}\cos(\tilde{\omega}t)\right] + \frac{2\Gamma\tilde{\omega}}{\tilde{\omega}^2 + \Gamma^2}\right\}.$$

Thus (12), which is the exponent of $I(\tau_1)$ in (9), is

$$-2i\left[\phi_s(\tau_2) - \phi_s(\tau_1 + \tau_2)\right],$$

and in (11) is

$$\phi(\tau) = -i\left[C\tau - \phi_s(\tau)\right] + \phi_R(\tau),$$

$$\phi_R(\tau) = \frac{C}{2\pi}\int_0^\infty \frac{d\omega}{\omega} A(\omega)\left[2N(\omega) + 1\right]\left[1 - \cos(\omega\tau)\right].$$

The real part of $\phi(\tau)$, called $\phi_R(\tau)$, was evaluated by direct numerical integration.

The absorption and emission were numerically evaluated using (6) and (8). The parts $\phi(\tau)$ and $I(\tau)$ were evaluated as just described, by including phonon damping and dispersion. The self energy term Σ_0 just equals C. There was no obvious value to take for the constant Γ. We tried the values $\Gamma \sim \omega_0$ and $\frac{1}{2}\omega_0$ and the two results were similar. Here we report the results for $\Gamma \sim \omega_0$. The other parameters are the same as listed earlier.

The results are shown in Fig. 4. The absorption is the solid line in Fig. 4(a). It is nearly identical in width and shape to the absorption shown in Fig. 2(a). This large value of phonon damping seems to have little affect upon the absorption spectra. A careful inspection shows that the peak position is shifted slightly to $-0.7\ \omega_0$.

Two emission spectra are also shown in Fig. 4(a). The one on the left-hand side has $\gamma = 0.0025$ eV which corresponds to a very long Auger decay time. The phonon ringing has time to completely decay away. Hence, the emission is the transition B in Fig. 3. The Franck-Condon shift has the expected value of $-2\Sigma_0 \simeq -12\omega_0$. This is the desired behavior, rather than the double-humped spectra of Fig. 2(a). This emission line is broader than the corresponding absorption line computed with the same parameters. It is also asymmetric in the wings.

The second emission line in Fig. 4(a) has $\gamma = 0.05$ eV, so that $\gamma \sim \omega_0 \sim \Gamma$. For this value, the emission line nearly overlaps the absorption. Further increasing γ seems to have little shape on the spectra—except broadening. For this value of γ the absorption at A in Fig. 3 is quickly followed by immediate emission, so the phonon system has little time to adjust. Hence, there is little Franck-Condon shift. This emission curve has two interesting features. First, it is broader than the corresponding absorption curve—by about 50%. This is not due to the increase in γ, but to some other feature. We are not sure whether it is the ringing of the phonons, or the phonon damping. The second feature is that there is a slight Franck-Condon between emission and absorption. This shift is about $-2\omega_0$. This value persists even as γ is raised. Indeed, it seems to occur for other parameter sets we have tried—all with strong phonon coupling. In metallic lithium, this would be a shift of about 0.1 eV. In fact, a small shift of this magnitude has been suggested, although the experimental situation is inconclusive at present.[4]

Figure 4(b) shows how the emission shifts from

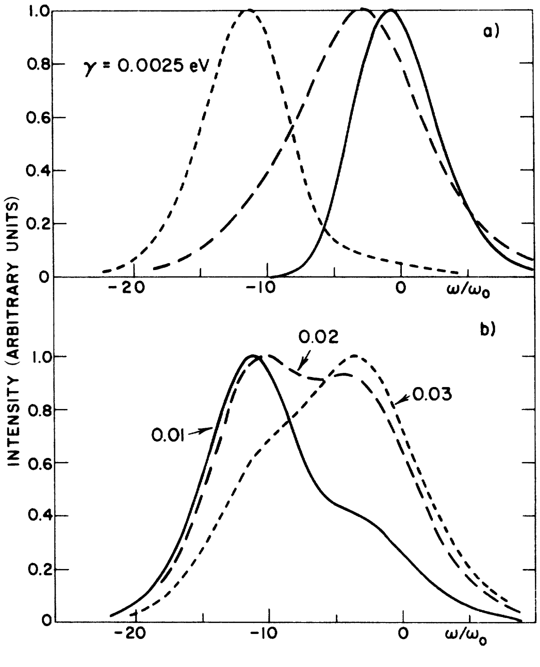

FIG. 4. Absorption and emission peaks arising from inclusion of phonon damping. (a) Solid line is absorption. Two dashed lines show emission for long-lived excited states ($\gamma = 0.0025$ eV) and short-lived excited states ($\gamma = 0.05$ eV). The former case has the expected Franck-Condon shift of $2\Sigma_0 \sim -12$ while the latter case does not. (b) Intermediate values of γ produce a double-humped emission spectra.

small values of γ to large ones. The emission peak does not shift. Instead, one peak grows and the other falls as γ is increased. In examining Fig. 4, it should be kept in mind that all emissions are arbitrary in intensity, so each has been normalized to the same peak height.

In summary, we have produced a theory that describes the Hedin model. If the hole lives a very long time, the phonon system has time to adjust and relax around it, and the emission does show a Franck-Condon shift of a nearly Gaussian shape. However, for very short hole lifetimes, the phonon system does not have time to adjust, and the Franck-Condon shift is much reduced. For intermediate times, we obtain a double-peaked spectra because of partial ringing effects. This is all affected by the rate at which the phonons damp out. Furthermore, the emission spectra always seem broader than the corresponding absorption calculated with the same parameters.

V. DISCUSSION

The reported core lifetime in lithium had a width (full width at half-maximum) of $\Gamma = 0.04 \pm 0.03$ eV.[5] Since $2\gamma = \Gamma$, then γ has the possible range of values from 0.005 to 0.035 eV. Figure 4(b) shows that this range of values spans the full range of relaxation. At $\gamma = 0.005$ eV, nearly full relaxation occurs, and there should be a Franck-Condon shift of 0.5 eV. For $\gamma = 0.35$ eV, little relaxation occurs, and only a small relaxation shift of 0.1 eV should occur. The preferred experimental value of $\gamma = 0.02$ eV is the intermediate behavior of a double-humped spectra. The spectral shapes we show would, in the absence of band-structure effects, be the derivative with frequency of the emission edge shapes. The self absorption corrections, which plague the emission data, would probably prevent the observation of this double-humped spectral shape. We can definitely conclude that the emission edge width is considerably larger than the absorption, which seems to be the situation experimentally. Lithium is the only metal with large reported phonon broadening of x-ray edge spectra. Such phenomena have been reported in polar insulators, and it would be worthwhile to examine the emission spectra of these cases.[17] These latter solids would be a good testing ground of the theory, and the best place to observe the behavior we have described.

In many simple metals, there sometimes exists significant electronic polarization and relaxation around the core hole. These give rise to the edge singularities, and related phenomena. Presumably the emission edge shape from electronic processes is also influenced by the degree of relaxation, and the relative size of the Auger width. This will be investigated next. However, these considerations should not affect the absorption edge data, which remain the primary testing ground of the edge singularity theory.

Note added in proof. T. A. Callcott and E. T. Arakawa, Phys. Rev. Lett. 38, 442 (1977) remeasured the emission spectra of metallic lithium. They found a Franck-Condon shift of 0.1 eV, in agreement with the present predictions. Their emission edge had a shoulder, which appears to be evidence for the behavior we predict in Fig. 4. We also received a private communication from C.-O. Almbladh, which reports results similar to those found here. Some related theoretical work has also been reported by P. Minnhagen, J. Phys. F 6, 1789 (1976), and M. Sunjic and A. Lucas, Chem. Phys. Lett. 42, 462 (1976).

ACKNOWLEDGMENTS

It is a pleasure to acknowledge helpful conversations with Professor William L. Schaich, who first provided the correct interpretation of the double-humped spectra.

APPENDIX

We wish to derive the general result for averages of L phonon operator products of the form

$$A = \langle X_1(t_1) X_2(t_2) \ldots X_L(t_L) \rangle$$

$$X_j(t_j) = \exp[M_j(b^\dagger e^{i\omega_0 t_j} - b e^{-i\omega_0 t_j})] .$$

These arise in the present theory as phonon coupling to states in a multiphoton process. We have also encountered them in the theory of the many small polaron problem.[15-17]

The Feynman theorem[13] is used to disentangle the exponent

$$X_j(t_j) = e^{-M_j^2/2} e^{M_j b^\dagger e^{i\omega_0 t_j}} e^{-M_j b e^{-i\omega_0 t_j}} ,$$

and the operators are successively commuted until all creation operators are on the left, and destruction operators on the right

$$A = \exp\left(-\tfrac{1}{2}\sum_{j=1}^{L} M_j^2 - \sum_{L \geq i > j \geq 1} M_i M_j e^{i\omega_0(t_i - t_j)}\right) \times \left\langle \exp\left(b^\dagger \sum_{j=1}^{L} M_j e^{i\omega_0 t_j}\right) \exp\left(-b \sum_{j=1}^{L} M_j e^{-i\omega_0 t_j}\right)\right\rangle .$$

Then the thermal average is simple, and yields
$\langle e^{\lambda b^\dagger} e^{-\lambda^\dagger b}\rangle = e^{-N|\lambda|^2}$,

$$A = \exp\left(-\tfrac{1}{2}\sum_{j=1}^{L} M_j^2 - \sum_{L \geq i > j \geq 1} M_i M_j e^{i\omega_0(t_i - t_j)} - N \times \sum_{i,j=1}^{L} M_i M_j e^{i\omega_0(t_i - t_j)}\right) .$$

The time-ordered product is also simple to obtain. It is, by inspection, simply

$$\langle TX_1(t_1)\cdots X_L(t_L)\rangle = \exp\left(-\tfrac{1}{2}\sum_{i=1}^{L} M_i^2 - \sum_{L\geq i>j\geq 1} M_i M_j e^{-i\omega_0|t_i-t_j|} - N\sum_{i,j=1}^{L} M_i M_j e^{i\omega_0(t_i-t_j)}\right).$$

These results were also obtained by Arnold.[19]

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*Research supported by a grant from the NSF.

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