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Effects of incomplete phonon relaxation on x-ray emission edges in simple metals*

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A theory for phonon broadening in x-ray emission is presented. The excitation and subsequent emission are treated as one quantum-mechanical process, within the Born-Oppenheimer approximation. The phonon part of the problem is exactly solvable for harmonic phonons with a linear coupling to the core hole. Explicit expressions for lifetime-dependent phonon broadening, line shape, and Stokes shift are given and calculated numerically for Li, Na, Al, and K. For long core-hole lifetimes the phonon broadening in x-ray absorption and in x-ray emission is the same, and there is a Stokes shift of twice the relaxation energy between the edges. When the lifetime becomes shorter the Stokes shift gradually disappears, and when the lifetime width Γ is comparable to the Debye energy there is an additional temperature-independent contribution to the phonon broadening, which may be called incomplete phonon relaxation. This effect is small for Al, but it should be present in the emission spectra from the alkalis provided Γ is in the right range. For Li, we obtain good agreement with both the observed Stokes shift and the emission edge shape reported recently by Callcott and Arakawa, and by Crisp, and the effect of incomplete phonon relaxation is likely to be the explanation of the longstanding problem of the broad Li emission edge. We also find indication that the effect is present in the emission spectra of Na and K.

I. INTRODUCTION

Before x-ray emission can take place, a core hole must first be created by, e.g., electron bombardment. A variety of "shakeup" excitations is created along with the core hole, and these excitations may interfere with the subsequent emission of the x-ray photon. Usually this interference is neglected and the emission experiment is treated as if the two steps of core-hole creation and x-ray emission were independent. It was recognized already by Skinner[1] that such an interference may occur, and qualitative discussions of this phenomenon have also been given in later reviews.[2-4]

A theoretical framework for describing the deep-level excitation and re-emission phenomena as one quantum-mechanical processes has been developed by Watts,[5] McMullen and Bergersen,[6] Yue and Donaich,[7] and the present author[8] and applied to shakeup excitations of the valence electrons. Watt's treatment was early and rather crude; McMullen and Bergersen applied the rather complicated Keldysh formalism,[9] as did Yue and Doniach. The present author, on the other hand, found a solution by using straightforward quantum-mechanical concepts involving only the well-known ideas that are used in resonance fluorescence.[10] This allows a rather transparent demonstration of the main features. The development in this paper is based on our earlier work.[8]

For long core-hole lifetimes the emission spectrum is given by a one-step process involving a fully relaxed initial state with a core hole, and is thus independent of how the core hole was created. For short core-hole lifetimes, on the other hand, deviations due to incomplete relaxation occur, and the size of these effects depends essentially (apart from a coupling constant) on the ratio Γ/B, where Γ is the core-hole lifetime width and B the bandwidth of the shakeup excitations under consideration.[8] B is a measure of how fast the excitations move away and $1/\Gamma$ of the time available for the excitations to disappear. Thus a large B/Γ means complete relaxation.

For shallow core levels in the simple metals Γ is very small (~10–20 meV) according to most estimates, and a very small effect of incomplete relaxation of the valence electrons is expected. The lifetime width Γ for these levels is, however, of the same order of magnitude as the phonon bandwidth, and it has been pointed out by McMullen and Bergersen[6] that the phonons have usually not relaxed when the x-ray emission takes place. A qualitative discussion of incomplete phonon relaxation has also been given by Hedin and Rosengren.[11] The present paper is devoted to a detailed investigation of these effects for simple metals, and results for phonon broadening, lifetime-dependent Stokes shift, and edge shapes are presented and compared with experiments.

In Sec. II we recapitulate and extend our earlier work[8] on reemission phenomena to include phonon effects within the framework of the Born-Oppenheimer approximation. The formalism involves basically second-order time-dependent perturbation theory where the Auger interaction and the coupling to the radiation field are treated as the perturbation. The unperturbed part of the Hamiltonian does not allow the core hole in the intermediate states to decay, and this causes the theory to diverge unless a self-energy renormalization of the resonant intermediate states is carried out. We indicate how this point can be justified formally on the basis of Heitler's theory[10] of resonance fluorescence.

The resulting expression for the cross section for core excitation and x-ray emission is obtained as a generalized Fourier transform of a correlation function

$$\hat{\Lambda}(t_1, t_2, t_3, t_4) = \langle T_1^\dagger(t_1) T_2(t_2) T_2^\dagger(t_3) T_1(t_4)\rangle$$

involving the transition operator for excitation (T_1) and emission (T_2) at four different times. In the Born-Oppenheimer approximation $\hat{\Lambda}$ factorizes in a purely electronic part and a phonon part.

When t_2 and t_3 are well separated from t_1 and t_4, $\hat{\Lambda}$ tends to an asymptotic limit where the excitation and emission processes are decoupled. This occurs, however, only in systems with infinitely many degrees of freedom and not in, e.g., an atom or a molecule. The asymptotic limit gives the dominant contribution for long core-hole lifetimes and corresponds to complete relaxation. The rate at which the system locally relaxes around the core-hole depends crucially on the dispersion of the excitations that couple to the core hole.

In Sec. III we evaluate the phonon part of the problem exactly in the case of harmonic phonons with a linear coupling to the core hole. We give explicit expressions for the core-level line shape, the lifetime-dependent Stokes shift, and the additional core-level width caused by the shakeup phonons from the initial excitation. The emission at threshold excitation is also discussed.

In Sec. IV we give numerical results for the lifetime-dependent phonon broadening for the simple metals Li, Na, Al, and K and compare these results with experiments. The phonon spectra and core-hole couplings from Ref. 11 are used. We find that incomplete phonon relaxation gives important additional broadening if the lifetime width Γ is of the same order of magnitude as the Debye energy. For the alkalies, Γ is in the right range to give important additional phonon broadening, while the effect for Al is quite small.

Section V, finally, contains a summary and conclusions.

II. THEORY

The total Hamiltonian H is split into an unperturbed part, H_0, containing all terms that conserve the number of core electrons and a perturbation. The perturbation consists of the Auger interaction H_A and the interaction with the radiation field, H_r. We study only the case when the uppermost core level is excited. Then, because of energy conservation, only one core level is involved in the dynamics. The extension to deeper core levels is simple but of no particular interest in the present context. We will also neglect the nonadiabatic interaction between the valence electrons and the phonons. The above assumptions are summarized in the Hamiltonian

$$H = H_0 + H_A + H_r. \tag{1}$$

The unperturbed part H_0 is

$$H_0 = H_v + H_{\text{ph}} + \epsilon_c b^\dagger b + b b^\dagger (V_v + V_{\text{ph}}) + H_{\text{phot}}. \tag{2}$$

The perturbation $H_A + H_r$ is given by

$$H_A = \sum_{\vec{p}} T_A(\vec{p}) c_{\vec{p}} b + \text{H.c.} \tag{3}$$

and

$$H_r = \sum_{\vec{q}\lambda} d_{\vec{q}\lambda} T_r(\vec{q}, \lambda) b + \text{H.c.} \tag{4}$$

Here H_v and H_{ph} are the valence electron and phonon Hamiltonians when all core levels are filled. The third term in H_0 is the core-electron energy; b is the annihilation operator for the core-level under consideration. V_v and V_{ph} are the additional terms when the core level is empty. H_{phot} finally represents the free radiation field. In the expressions for H_A and H_r, $c_{\vec{p}}$ and $d_{\vec{q}\lambda}$ are the annihilation operators for the fast electron and the x-ray photon, respectively. $T_A(\vec{p})$ and $T_r(\vec{q}, \lambda)$ contain only valence electron operators and are given by

$$T_A(\vec{p}) = \frac{1}{2} \sum_{\vec{k}\vec{k}'} (\langle \vec{k}\vec{k}' | v | c\vec{p}\rangle - \langle \vec{k}\vec{k}' | v | \vec{p}c\rangle) c_{\vec{k}}^\dagger c_{\vec{k}'}^\dagger, \tag{5}$$

and

$$T_r(\vec{q}, \lambda) = (2\pi\alpha/q)^{1/2} \sum_{\vec{k}} \langle \vec{k} | -i\nabla/m | c\rangle c_{\vec{k}}^\dagger \tag{6}$$

in terms of core-valence matrix elements of the Coulomb interaction v and the momentum. α is the fine-structure constant. For simplicity the spin indices are suppressed, and we use units such that $\hbar = 1$.

In an electron-excited emission process, for example, we start from an initial state $c_{\vec{p}}^\dagger | 0\rangle$ where the target is in its ground state $|0\rangle$ and the incident electron has a momentum $\vec{p}$. We study transitions to final states $d_{\vec{q}\lambda}^\dagger | s\rangle$ with an emitted photon $\vec{q}\lambda$, the core level filled, and the crystal being in some excited state $|s\rangle$. For these resonant phenomena the usual second-order time-dependent perturbation theory is divergent, and an extension[12] corresponding to Heitler's theory of resonance fluorescence[10] must be applied. The transition rate to the final states of interest is then given by

$$W(\vec{p}, \vec{q}\lambda) = 2\pi \sum_s |M(\vec{q}\lambda, s; \vec{p}, 0)|^2 \times \delta(E_s + \Omega_q - E_0 - \epsilon_p), \tag{7}$$

where

$$M(\vec{q}\lambda, s; \vec{p}, 0) = \sum_r \frac{\langle s | d_{\vec{q}\lambda} H_r | r^* \rangle \langle r^* | H_A c^\dagger_{\vec{p}} | 0 \rangle}{E_s + \Omega_q - E_r^* + \frac{1}{2} i \Gamma} . \tag{8}$$

Here ϵ_p and Ω_q are the energies of the incident electron and the emitted photon, respectively, and E_s and E_r^* are energy eigenvalues for the target. States with empty core level are indicated by an asterisk. Nonresonant intermediate states with filled core level are neglected in Eq. 8. The lifetime width Γ in this theory comes from a partial summation in the equations of motion, and in this way a self-energy correction to each state $|r^*\rangle$ is obtained. In order to arrive at Eqs. (7) and (8) we must further assume that this self-energy varies little over the energy range where shakeup excitations are important (this is particularly well satisfied for phonons). It can then be replaced by its value at the core-electron binding energy. The real part may be absorbed in ϵ_c, and the imaginary part gives in the usual way a damping Γ.

As was stressed in our earlier work,[8] only processes that contribute to the core-hole annihilation should be included in this self-energy summation. All other terms, such as, e.g., interactions between the core-hole and particle-hole pairs, and with phonons, should be included in H_0. These latter interactions contribute to the decay of the core-electron Green's function but not to the annihilation rate.[6, 8] It is this latter quantity that determines the time available for the core hole to relax in the emission process. It is thus incorrect to include, e.g., phonon broadening in the parameter Γ. The present analysis shows that although the phonons contribute to the core-level width, they do not influence the degree of relaxation in the electronic part of the problem.

In Eq. 8 the photons disappear trivially, and the first matrix element is simply $\langle s | b^\dagger T_r^\dagger(\vec{q}, \lambda) | r^* \rangle$. We will also neglect extrinsic effects (energy losses) associated with the incident electron; the second matrix element in Eq. (8) is then simplified to $\langle r^* | T_A(\vec{p}) b | 0 \rangle$. Finally, we transform the summation over eigenstates of H_0 to a product of Heisenberg operators in the usual way and obtain

$$\begin{aligned} W(\vec{p}, \vec{q}\lambda) &= \int_{-\infty}^{\infty} d\tau \int_0^{\infty} dt\, dt' \exp\{ i [-\Omega_q (t - t') + (\epsilon_p - \Omega_q)\tau] \\ &\qquad - \tfrac{1}{2}\Gamma(t + t') \} \\ &\qquad \times \hat{\Lambda}_{\vec{p}, \vec{q}\lambda}(\tau, t + \tau, t', 0) , \end{aligned} \tag{9}$$

where

$$\begin{aligned} \hat{\Lambda}_{\vec{p}, \vec{q}\lambda}(t_1, t_2, t_3, t_4) &= \langle b^\dagger(t_1) T_A^\dagger(\vec{p}, t_1) T_r(\vec{q}\lambda, t_2) b(t_2) \\ &\qquad \times b^\dagger(t_3) T_r^\dagger(\vec{q}\lambda, t_3) T_A(p, t_4) b(t_4) \rangle . \end{aligned} \tag{10}$$

Expressions for x-ray excited spectra are derived in a similar way, and the result is obtained from Eqs. (9) and (10) by replacing ϵ_p by the energy $\Omega_{q'}$ for the incident photon and $T_A(\vec{p})$ by $T_r(\vec{q}', \lambda')$. When the target has a temperature $T > 0$, the average in Eq. (10) should be taken over the canonical ensemble rather than the ground state.

Equations (9) and (10) provide the basic theoretical framework for describing deep-level absorption and reemission phenomena, and the formalism is considerably more complicated than the linear-response theory that is used for describing absorption spectra. The theory can be extended to include the dynamics of more than one core level, and it is then applicable to, e.g., resonant Raman x-ray scattering[13, 14] involving transitions from deeper to more shallow core levels, and to Auger K-LL spectra.[15]

The key quantity $\hat{\Lambda}$ can be evaluated exactly in some important model cases; one such model consists of independent bosons with a linear coupling to the core hole. In the general case, however, one has to resort to methods like those developed by Keldysh,[9] since the correlation $\hat{\Lambda}$ is not time ordered.

As remarked earlier, in the limit $t_2, t_3 \to \infty$ for fixed t_1 and t_4, we have asymptotically a factorization

$$\begin{aligned} \hat{\Lambda}_{\vec{p}, \vec{q}\lambda}(t_1, t_2, t_3, t_4) &\sim \langle b^\dagger(t_1) T_A^\dagger(\vec{p}, t_1) T_A(\vec{p}, t_4) b(t_4) \rangle \\ &\qquad \times \langle T_r(\vec{q}\lambda, t_2) b(t_2) b^\dagger(t_3) T_r^\dagger(\vec{q}\lambda, t_3) \rangle_* . \end{aligned} \tag{11}$$

In the Appendix we give a general argument for why this factorization occurs. The asterisk is used to indicate that the average in the second factor should be taken over an ensemble corresponding to a system in equilibrium with the core hole. Usually a correlation function like the one in Eq. (10) is local in its time variables for systems with infinitely many degrees of freedom in the sense that the correlation tends to zero when the time separation between any of the time coordinates tends to infinity. Our correlation $\hat{\Lambda}$ in Eq. (10) differs from this behavior, and Eq. (11) reflects that H_0 does not allow the core hole to disappear.

As was stated in the Introduction, the limit in Eq. (11) implies that the excitation and the reemission events are independent for long core-hole lifetimes; it also implies the necessity of taking the decay of the intermediate states into account.

The Fourier transform of the first factor in Eq. (11) is the excitation cross section

$$\Lambda^{a}_{\vec{p}}(\omega)=\int dt\,\langle b^{\dagger}(t)T^{\dagger}_{A}(\vec{p},t)T_{A}(\vec{p},0)b(0)\rangle\, e^{i\omega t}, \tag{12}$$

and the emission rate from the fully relaxed core-hole is obtained in a similar way from the second factor,

$$\Lambda^{e}_{\vec{p}\lambda}(\omega)=\int dt\,\langle T_{r}(\vec{q}\lambda,t)b(t)b^{\dagger}(0)T^{\dagger}_{r}(\vec{q}\lambda,0)\rangle_{*}\times e^{-i\omega t}. \tag{13}$$

When $\Gamma\rightarrow 0$, the contribution from the transient part in $\hat{\Lambda}$ tends to zero in comparison with that from the asymptotic tail in Eq. (11). Thus, for small Γ we can neglect the transients; the total process is then given by a simple rate equation,

$$W^{\infty}(\vec{p},\vec{q}\lambda)=\int\frac{d\omega}{2\pi}\,\frac{\Lambda^{a}_{\vec{p}}(\epsilon_{p}-\Omega_{q}+\omega)\Lambda^{e}_{\vec{q}\lambda}(\omega)}{(\omega-\Omega_{q})^{2}+\frac{1}{4}\Gamma^{2}}$$

$$\sim\Lambda^{a}_{\vec{p}}(\epsilon_{p})(1/\Gamma)\Lambda^{e}_{\vec{q}\lambda}(\Omega_{q})\quad(\Gamma\rightarrow 0). \tag{14}$$

Γ is the decay rate in all available (Auger and radiative) channels, and we notice that the total x-ray yield per excited core level is Γ_{r}/Γ as it should (Γ_{r} is the radiative part of Γ).

We now turn to the phonons. When taking the thermal average in Eq. (10), we can neglect thermal fluctuations in the core-level occupation number. The density matrix ρ can thus be restricted to the subspace corresponding to filled core levels, and its explicit form is ($\beta=1/kT$)

$$\rho(T)=\exp[\beta(F_{v}-H_{v})]\exp[\beta(F_{\text{ph}}-H_{\text{ph}})],$$

where F_{v} and F_{ph} are the valence-electron and the phonon parts of the free energy, respectively. Each Heisenberg operator in Eq. (10) consists of a transition operator involving only the electrons, multiplied with the appropriate time evolution operators. Since no interaction between the valence electrons and the phonons is included in H_{0}, the evolution operator is made up of two commuting factors corresponding to the electrons and to the phonons. This is valid both when the core level is filled and when it is empty. $\hat{\Lambda}$ is thus obtained as a simple product, $\hat{\Lambda}=\hat{\Lambda}_{v}\times\hat{\Lambda}_{\text{ph}}$, in a self-explanatory notation.

The phonon part is given by

$$\hat{\Lambda}_{\text{ph}}(t_{1},t_{2},t_{3},t_{4})=\langle U^{\dagger}_{0}(t_{1})U_{1}(t_{1}-t_{2})U_{0}(t_{2}-t_{3})U_{1}(t_{3}-t_{4})U_{0}(t_{4})\rangle \tag{15}$$

in terms of the evolution operators for the phonons, $U_{0}(t)=\exp(-itH_{\text{ph}})$ and $U_{1}(t)=\exp[-it(H_{\text{ph}}+V_{\text{ph}})]$. The valence-electron part, $\hat{\Lambda}_{v}$, may be replaced by its asymptotic limit in Eq. (11), since $1/\Gamma$ is large compared to the electronic relaxation time for the shallow core levels discussed here. The probability for core-level excitation and x-ray emission in Eq. (9) is then simplified to

$$W(\vec{p},\vec{q}\lambda)=\int\frac{d\omega_{1}d\omega_{2}}{(2\pi)^{2}}\,\Lambda^{a}_{v\vec{p}}(\omega_{1})\Lambda^{e}_{v\vec{q}\lambda}(\omega_{2})\times\Lambda_{\text{ph}}(\epsilon_{p}-\omega_{1},\Omega_{q}-\omega_{2};\Gamma). \tag{16}$$

In the above expression Λ_{ph} is given by

$$\Lambda_{\text{ph}}(\omega_{1},\omega_{2};\Gamma)=\int_{-\infty}^{\infty}d\tau\int_{0}^{\infty}dt\,dt'\,\hat{\Lambda}_{\text{ph}}(\tau,t+\tau,t',0)\times\exp[i(\omega_{1}-\omega_{2})\tau-i\omega_{2}(t-t')-\tfrac{1}{2}\Gamma(t+t')]. \tag{17}$$

$\Lambda^{a}_{v\vec{p}}(\omega)$ and $\Lambda^{e}_{v\vec{q}\lambda}(\omega)$ are the valence-electron parts of the probabilities for excitation and x-ray emission in Eqs. (12) and (13).

When the target is excited with particles of an energy well above the threshold, Eq. (16) can be simplified further. The phonon part Λ_{ph} is as a function of ω_{1} sharply peaked around zero frequency, with a width of the same order of magnitude as the phonon broadening of the core level (see Sec. III). We can therefore replace the full Λ_{ph} by the approximation

$$C(\omega_{2},\Gamma)\delta(\omega_{1})=\delta(\omega_{1})\int\frac{d\omega}{2\pi}\,\Lambda_{\text{ph}}(\omega,\omega_{2};\Gamma).$$

Equation (16) is then simplified to

$$W(\vec{p},\vec{q}\lambda)\equiv\Lambda^{a}_{v\vec{p}}(\epsilon_{p})\int\frac{d\omega}{2\pi}\,\Lambda^{e}_{v\vec{q}\lambda}(\omega)C(\Omega_{q}-\omega,\Gamma). \tag{18}$$

The emission spectrum is now given as convolution of a purely electronic part $I^{e}_{v}(\omega)$, obtained by averaging $\Lambda^{e}_{v\vec{q}\lambda}$ over $\vec{q}$ and λ, with a generalized phonon and lifetime broadening function $C(\omega,\Gamma)$. The excitation probability $\Lambda^{a}_{v\vec{p}}$ factorized out. The broadening C is given by

$$C(\omega,\Gamma)=\int dt\,dt'\,\hat{\Lambda}_{\text{ph}}(0,t,t',0)\times\exp[-i\omega(t-t')-\tfrac{1}{2}\Gamma(t+t')]. \tag{19}$$

Equations (18) and (19) correspond closely to the treatment in Refs. 5–7.

In the approximation corresponding to Eq. (18) the effect of the initial excitation on the phonons is described as a sudden removal of the core electron at $t=0$. Thus, the effects of incomplete phonon relaxation are the same in both x-ray excited and electron excited spectra in the limit where Eq. (18) is applicable. Close to threshold, however, the probability for excitation by electron bombardment tends to zero as $\epsilon-\epsilon_{c}$, while the cross section for excitation by x rays starts with a Fermi edge. The two modes of excitation may therefore give different results at threshold excitation when incomplete relaxation effects are important. We will return to the emission at threshold excitation in Sec. III.

III. EVALUATION OF PHONON EFFECTS IN THE HARMONIC APPROXIMATION

In order to proceed further we must specify the phonon Hamiltonian, and we adopt the model of harmonic phonons with a linear coupling to the core hole[4, 11, 16]:

$$H_{\mathrm{ph}}=\sum_n \omega_n a_n^\dagger a_n\,, \tag{20}$$

and

$$V_{\mathrm{ph}}=\sum_n B_n (a_n+a_n^\dagger)\,. \tag{21}$$

Here a_n is a phonon operator, and ω_n and B_n are the frequency and the coupling constant for the phonon mode n. Within this model the phonon part of the problem is exactly solvable with a method used by Langreth.[17] The perturbed Hamiltonian $H_{\mathrm{ph}} + V_{\mathrm{ph}}$ is diagonalized by the unitary transformation

$$S=\exp\left(\sum_n \frac{B_n}{\omega_n}(a_n-a_n^\dagger)\right)\,.$$

By applying this transformation to each factor U_1 in Eq. (15) we find

$$U_1(t)=S^\dagger U_0(t) S\exp(i\epsilon_0 t)$$

and

$$\hat\Lambda_{\mathrm{ph}}(t_1,t_2,t_3,t_4)=\langle S^\dagger(t_1)S(t_2)S^\dagger(t_3)S(t_4)\rangle \times\exp[i\epsilon_0(t_1-t_2+t_3-t_4)]\,. \tag{22}$$

ϵ_0 is given below. When evaluating Eq. (22) we may consider one phonon mode at a time, and we temporarily drop the mode index n. The product of the four Heisenberg operators of the form

$$S(t)=U_0^\dagger(t)SU_0(t) =\exp[(B/\omega)(ae^{-i\omega t}-a^\dagger e^{i\omega t})]$$

can be simplified to

$$S^\dagger(t_1)S(t_2)S^\dagger(t_3)S(t_4)=e^\alpha\exp(\beta a+\gamma a^\dagger)$$

by making multiple use of the relation[18]

$$\exp(A)\exp(B)=\exp(A+B+\tfrac12[A,B])\,.$$

The thermal average is then obtained with aid of the formula[18]

$$\langle\exp(\beta a+\gamma a^\dagger)\rangle=\exp(\beta\gamma\langle a^\dagger a+\tfrac12\rangle).$$

The final result for $\hat\Lambda_{\mathrm{ph}}$ is

$$\hat\Lambda_{\mathrm{ph}}(t_1,t_2,t_3,t_4) =\exp[i\epsilon_0(t_1-t_2+t_3-t_4)+f(t_4-t_1)+f(t_3-t_2) +f(t_2-t_1)-f(t_4-t_2)-f(t_3-t_1)+f(t_4-t_3)]\,, \tag{23}$$

where[4, 11, 16]

$$\epsilon_0=\int_0^\infty d\omega\,\omega g(\omega)\,, \tag{24}$$

$$f(t)=\int_0^\infty d\omega\, g(\omega)\{[2n(\beta\omega)+1](\cos\omega t-1)+i\sin\omega t\}\,, \tag{25}$$

$$g(\omega)=\sum_n |B_n/\omega_n|^2\delta(\omega-\omega_n), \tag{26}$$

and

$$n(\beta\omega)=1/(e^{\beta\omega}-1)\,. \tag{27}$$

In Eq. (23), which is the generalization of Eq. (21) in Ref. 8 to finite temperatures, the first three terms in the exponent depend only on t_1-t_4 and t_2-t_3 and correspond to complete relaxation. The remaining terms are the transients which contribute for short core-hole lifetimes. It is evident from Eq. (25) that the time scale for the phonon relaxation, i.e., the decay rate of the transients, is given by the inverse bandwidth rather than the time for a lattice vibration. When the bandwidth is zero no relaxation occurs.[19]

We first consider the case when the core-level is excited with radiation of an energy well above threshold. The phonon effects are now described by

$$\hat\Lambda_{\mathrm{ph}}(0,t,t',0)=\exp\{-i\epsilon_0(t-t')+f(t'-t) +2i[f_2(t)-f_2(t')]\}, \tag{28}$$

where $f_2(t)$ is the temperature-independent imaginary part of $f(t)$.

In the following analysis it is convenient to split off a Lorentzian from the total broadening $C(\omega,\Gamma)$ in Eq. (19) and define a new broadening function D by

$$\Gamma C(\omega,\Gamma)=\int\frac{d\omega'}{2\pi}D(\omega',\Gamma)\frac{\Gamma}{(\omega-\omega')^2+\frac14\Gamma^2}\,, \tag{29}$$

and after a few simple transformations we obtain

$$D(\omega,\Gamma)=\int dt\,\hat D(t,\Gamma)e^{-i\omega t}, \tag{30}$$

where

$$\hat D(t,\Gamma)=\Gamma\exp(\tfrac12\Gamma|t|) \times\int_{|t|/2}^\infty d\tau\,\hat\Lambda_{\mathrm{ph}}(0,\tau+\tfrac12 t,\tau-\tfrac12 t,0)e^{-\Gamma\tau}\,. \tag{31}$$

In the limit $\Gamma \to 0$, $\hat{D}(t, \Gamma)$ reduces to

$$\hat{D}(t, 0) = \langle U_1^\dagger(t) U_0(t) \rangle_* = \exp[-i\epsilon_0 t + f(-t)], \quad (32)$$

i.e., the phonon broadening function in the ordinary theory of x-ray emission, in accordance with the discussion in Sec. II. The asterisk indicates as usual that the average in Eq. (32) is taken over an ensemble where the phonons are in equilibrium with the core hole. In this limit the first frequency moments of D are

$$\langle \omega \rangle = -2\epsilon_0, \quad (33)$$

$$\langle \omega^2 \rangle - \langle \omega \rangle^2 \equiv \Delta^2(T) = \int_0^\infty d\omega\, \omega^2 g(\omega)[2n(\beta\omega) + 1], \quad (34)$$

and the absorption and emission edges are Stokes shifted with an amount $2\epsilon_0$ and are of the same widths.

In the other limit, when Γ is large compared to a typical phonon frequency, only small t and t' are important in Eq. (19) for the total broadening function $C(\omega, \Gamma)$. In this limit $\Gamma C(\omega, T)$ is reduced to a convolution of the phonon broadening $D_a(\omega)$ for absorption with a Lorentzian $\Gamma/(\omega^2 + \frac{1}{4}\Gamma^2)$. $D_a(\omega)$ is the Fourier transform of[4, 11, 16]

$$\hat{D}_a(t) = \langle U_1^\dagger(t) U_0(t) \rangle = \exp[-i\epsilon_0 t + f(t)], \quad (35)$$

and has the moments $\langle \omega \rangle = 0$ and $\langle \omega^2 \rangle = \Delta^2(T)$. In this limit there is no Stokes shift between the emission and absorption edges, and their widths are again the same. Since only small values of t are involved in Eqs. (19) and (35), no finer details of the phonon dynamics are resolved, and the emission and absorption edges merely reflect the statistical fluctuations in the instantaneous positions of the ions surrounding the atom that is being excited. The phonon broadening may also in this case be comparable or larger than Γ, since in many cases several shakeup phonons are involved (see Sec. IV, Table I).

In the intermediate range, when Γ is comparable to the phonon bandwidth, there will be a Γ-dependent Stokes shift and an extra width Δ_Γ from shakeup phonons. The moments $\langle \omega^n \rangle_\Gamma$ of $D(\omega, \Gamma)$ in Eq. (30) are obtained in the usual way by differentiating $\hat{D}(t, \Gamma)$ with respect to t, and a simple calculation yields

$$\langle \omega \rangle_\Gamma = -2\epsilon_0 + 2\int_0^\infty dt\, \Gamma e^{-\Gamma t} f_2'(t) = -2\epsilon_0 + 2\int_0^\infty d\omega\, \omega g(\omega) \frac{\Gamma^2}{\omega^2 + \Gamma^2}, \quad (36)$$

$$\langle \omega^2 \rangle_\Gamma - \langle \omega \rangle_\Gamma^2 = \Delta^2(T) + \Delta_\Gamma^2, \quad (37)$$

where

$$\Delta_\Gamma^2 = 4\int_0^\infty dt\, \Gamma e^{-\Gamma t}[f_2'(t)]^2 - 4\left(\int_0^\infty dt\, \Gamma e^{-\Gamma t} f_2'(t)\right)^2$$
$$= 2\int_0^\infty d\omega d\omega'\, \omega\omega' g(\omega) g(\omega') \times \left(\frac{\Gamma^2}{(\omega + \omega')^2 + \Gamma^2} + \frac{\Gamma^2}{(\omega - \omega')^2 + \Gamma^2} - \frac{2\Gamma^4}{(\omega^2 + \Gamma^2)(\omega'^2 + \Gamma^2)}\right). \quad (38)$$

It may be noticed that the lifetime-dependent Stokes shift $\langle \omega \rangle_\Gamma$ and the additional width Δ_Γ are independent of T and that they fulfill the limits stated in the preceding paragraphs. The first line in Eq. (38) also implies $\Delta_\Gamma^2 \geq 0$.

It is seen from Eq. (36)–(38) that $\langle \omega \rangle_\Gamma$ depends essentially on the center of gravity of $\omega g(\omega)$, while Δ_Γ is also sensitive to the spread in the phonon distribution. For acoustic phonons both the mean phonon energy and the spread in the phonon distribution are approximately the same as the Debye energy ω_D, and the effect of incomplete phonon relaxation are thus largest when $\Gamma \sim \omega_D$.

When the core hole is created by particles of an energy close to the threshold, the approximation in Eq. (18) is not valid, and we must go back to the full expressions in Eqs. (16) and (17). The calculation of $\Lambda_{\text{ph}}(\omega_1, \omega_2; \Gamma)$ is in principle simple but time consuming, since the evaluation involves a three-dimensional integral with, say, 200 mesh points in each direction for each value of ω_1, ω_2 and Γ. However, some conclusions can be drawn without numerical work.

We first remark that the phonon part $\Lambda_{\text{ph}}(\omega_1, \omega_2; \Gamma)$ in Eq. (17) is non-negative. In order to estimate the range in ω_1 where it is non-negligible we integrate over ω_2:

$$\int \frac{d\omega_2}{2\pi} \Lambda_{\text{ph}}(\omega_1, \omega_2; \Gamma) = \int_0^\infty dt\, dt' \exp[i\omega_1(t' - t) - \tfrac{1}{2}\Gamma(t + t')] \hat{D}_a(t - t') = (1/\Gamma)\int_{-\infty}^\infty dt\, \exp[-i\omega_1 t - \tfrac{1}{2}\Gamma|t|] \hat{D}_a(t). \quad (39)$$

By also integrating over ω_1 we find the sum rule

$$\int \frac{d\omega_1 d\omega_2}{(2\pi)^2} \Lambda_{\text{ph}}(\omega_1, \omega_2; \Gamma) = 1/\Gamma. \quad (40)$$

Note that the harmonic approximation need not be invoked in the derivation of Eqs. (39) and (40). The right-hand side of Eq. (39) is just the usual phonon broadening $D_a(\omega)$ for absorption, convoluted with a Lorentzian with a full width at half maximum (FWHM) Γ, multiplied with $1/\Gamma$. The factor $1/\Gamma$ enters because the electronic parts in the (Auger and radiative) decay channels have been sorted out. From Eq. (39) we conclude that the phonon effects in emission can be affected by the energy of the incident particle only when this energy is within a few phonon broadening widths Δ from the threshold. It is also interesting to notice that the absorption spectrum is always described by the same phonon broadening function $D_a(\omega)$, convoluted with a Lorentzian of the appropriate width, and not affected by the degree of relaxation in the emission process.

It is also of interest to study the phonon response to the *total* process of core-hole creation and subsequent emission. Evidently, for short core-hole lifetimes the phonons cannot be affected by the deep-level process. The energy distribution of the phonons after the x-ray emission is described by the variable $\Omega=\omega_1-\omega_2$ in $\Lambda_{\text{ph}}(\omega_1,\omega_2;\Gamma)$. Physically, this is obvious, since ω_1 corresponds to the energy that is absorbed by the phonons in the excitation process, and $-\omega_2$ to the energy given to the phonons in the subsequent emission. Mathematically, it follows from Eqs. (15) and (17), since Ω corresponds to Fourier transformation with respect to τ and thus to the summation over final states $|s\rangle$ in Eq. (7).

When Γ is small, the emission spectrum is clearly independent of the energy of the incident radiation down to the excitation threshold [see Eq. (14)]. Since the two steps of excitation and x-ray emission are independent in this limit, the mean energy that is absorbed by the phonons in the total process is

$$\int\frac{d\omega}{2\pi}\,\omega D_a(\omega)-\int\frac{d\omega}{2\pi}\,\omega D(\omega,0)=2\epsilon_0\,.$$

In fact, we have generally

$$\langle\Omega\rangle=\Gamma\int\frac{d\omega_1d\omega_2}{(2\pi)^2}(\omega_1-\omega_2)\Lambda_{\text{ph}}(\omega_1,\omega_2;\Gamma)=-\langle\omega\rangle_\Gamma\,, \tag{41}$$

where $\langle\omega\rangle_\Gamma$ is given in Eq. (36). Thus the energy that is absorbed by the phonons in the total process tends to zero as $-\langle\omega\rangle_\Gamma$ when $\Gamma\to\infty$. Equation (41) follows from the relations in Eqs. (19) and (39) between Λ_{ph} and the phonon broadenings for emission and for absorption, and from the fact that a convolution with a Lorentzian does not change the first moment.

The second moment with respect to Ω is obtained by differentiating $\Lambda_{\text{ph}}(\tau,t+\tau,t',0)$ with respect to τ. The calculation is elementary, so we just quote the result,

$$\langle\Omega^2\rangle-\langle\Omega\rangle^2=2\Delta^2(T)+\Delta_\Gamma^2-2\int_0^\infty d\omega\,\omega^2g(\omega)\times[2n(\beta\omega)+1]\frac{\Gamma^2}{\omega^2+\Gamma^2}\,. \tag{42}$$

The energy spread of the phonons after the total process tends to $\sqrt{2}$ when $\Gamma\to0$, and it tends to zero in the other limit $\Gamma\to\infty$. The first term in the right-hand side of Eq. (42) represents the energy spread of the phonons if they independently had been subject to the sudden potential changes $\pm V_{\text{ph}}$, the second term is the additional contribution to the emission broadening, and the third term is a cross term. It is also possible to show explicitly that, in the limit $\Gamma\to\infty$, the phonons have a unit probability of returning to the initial state after the x-ray emission. Thus the present theory correctly describes the limiting case $\Gamma\to\infty$.

At first sight it is somewhat surprising that the phonon contribution to the core-level width in absorption does not depend on Γ in spite of the fact that the phonons are unaffected by the deep-level process in the limit $\Gamma\to\infty$. The apparent contradiction is resolved by the fact that, in the limit $\Gamma\to\infty$, the energy spread of the phonons in the intermediate states with an empty core level is transferred to the emitted x-ray photon or Auger electron in the subsequent step.

At zero temperature $\Lambda_{\text{ph}}(\omega_1,\omega_2;\Gamma)$ is nonzero only when $\omega_1\geq\omega_2$. This relation is exactly fulfilled, and no lifetime broadening is involved in the total process. At finite temperatures, $\Lambda_{\text{ph}}(\omega_1,\omega_2;\Gamma)$ is non-negligible only when $\omega_1\gtrsim\omega_2-kT$. For shorter core-hole lifetimes, when the Stokes shift in emission is partially quenched, the center of gravity of the phonon broadening function for emission must therefore move to lower energies and the broadening must be sharpened when the energy of the incident radiation approaches the threshold. Spectra recorded at threshold excitation would therefore be of high interest.

IV. RESULTS AND COMPARISON WITH EXPERIMENTS

In order to get quantitative numbers for the lifetime-dependent broadening in emission a realistic calculation of $g(\omega)$ is needed. Detailed calculations have been made by Bergersen *et al.*[16] and by Hedin and Rosengren.[11] The evaluation of phonon broadening involves calculations of the phonon spectrum and of the coupling constants B_n in Eq. (21). Since the Hamiltonian that is used in Refs. 4, 11, and 16 corresponds to the Born-Oppenheimer approximation [see Eq. (2)], the phonon coupling is determined by the core-electron binding energy $-\epsilon_c(\vec{R}_i)$ as a function of the nuclear positions $\{\vec{R}_i\}$. The main difference between Hedin's approach[4] and that of Bergersen *et al.*[16] concerns the treatment of this quantity.

In the approach of Bergersen *et al.*[16] the $\vec{R}_i$-dependent part of ϵ_c is given as the potential energy of point charges at the positions $\vec{R}_i$ in the field from a linearly screened, bare Coulomb potential from the core hole. However, recent *ab initio* calculations of core-hole potentials[20] and point-charge screening[21] show that the core-hole potential is quite different from the potential from a screened point charge. Inside the central cell the induced Hartree potentials differ by a factor of 2, and outside the central cell the phases of the Friedel oscillations are different.

In Hedin's approach[4] explicit reference to the core-hole potential is avoided, and his analysis starts from the expression[22,23]

$$\epsilon_c(\vec{R}_i) = \epsilon_{\text{ion}} + V_H(\vec{R}_i) + \tfrac{1}{2} V_p , \qquad (43)$$

where $-\epsilon_{\text{ion}}$ is the core-level binding energy for the free ion, and $V_H(\vec{R}_i)$ is the Hartree potential from the valence electrons and surrounding ions in the (electronic) ground state. V_p is the polarization potential induced by the core hole. The range of validity of Eq. (43) is fairly well understood, and the neglected terms involve mainly (i) a slight change in the core-electron wave function when the ion is put in a solid, (ii) core-valence exchange, and (iii) nonlinear polarization effects. The neglected terms amount to 1–2 eV for simple metals,[20] but they should change little with a slight change of the nuclear positions $\vec{R}_i$, and we feel that Hedin's approach is more accurate than that of Bergersen *et al.* The data from Hedin and Rosengren's calculation were therefore used in the present work.

The lifetime-dependent quantities $\langle \omega \rangle_\Gamma$ and Δ_Γ in Eqs. (36)–(38) were calculated numerically for Li, Na, Al, and K. In these calculations, the ω integration was transformed to an integration over the Brillouin zone (BZ) according to the prescription

$$\int d\omega\, g(\omega) = \frac{1}{16\pi^3 \rho} \int_{\text{BZ}} d^3q\, |F_{\vec{q}\lambda}|^2 \frac{1}{\omega^3_{\vec{q}\lambda}} \;,$$

in the notation of Ref. 11. The resulting integrals over the Brillouin zone were evaluated with Bansil's method[24] using five directions and ten points in each direction. For Li, calculations were also made with 13 directions, and the results obtained with the different numbers of mesh points indicated a numerical accuracy of the order 0.1% for $\langle \omega \rangle_\Gamma$, Δ_Γ, and the line shapes. The calculation of $\omega_{\vec{q}\lambda}$ and $F_{\vec{q}\lambda}$ is described in Ref. 11.

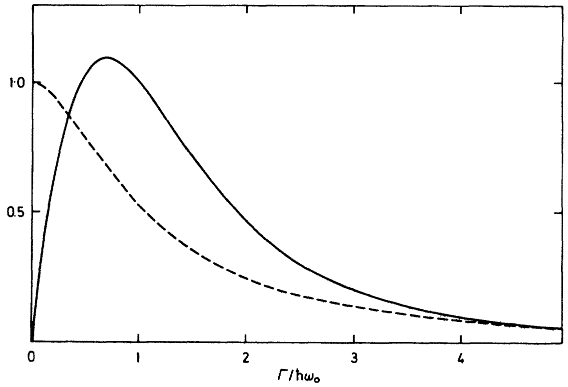

FIG. 1. Lifetime-dependent part Δ_Γ of the phonon broadening in emission and the Stokes shift $\hbar\langle \omega \rangle_\Gamma$ for different values of Γ. The curves correspond to the model in Eq. (44). The solid curve gives $\Delta_\Gamma^2/\epsilon_0'^2$, and the dashed curve gives $-\hbar\langle \omega \rangle_\Gamma / 2\epsilon_0'$ as a function of $\Gamma/\hbar\omega_0$. The values of ϵ_0' and $\hbar\omega_0$ for Li, Na, Al, and K are given in Table I.

TABLE I. Values for ϵ_0' and $\hbar\omega_0$ obtained by fitting the model results corresponding to Eq. (44) to the results from the numerical calculations. The number of shake-up phonons $\bar{n}(0)$ at $T=0$ K, the relaxation energy ϵ_0, and the standard deviation $\Delta(0)$ of the phonon broadening at $T=0$ K without incomplete relaxation effects are also given. Energies in meV.

Element	$\hbar\omega_0$	ϵ_0'	$\bar{n}(0)$	ϵ_0	$\Delta(0)$
Li	20.5	112	6.0	110	50.1
Li[a]	20.5	263	14	257	76.7
Na	8.3	82	10.9	80	27.4
Al	20.6	15	0.58	13	18.0
K	5.3	81	16.4	79	21.7

[a] Rescaled core-hole coupling; see text.

The numerical results for $\langle \omega \rangle$ and Δ_Γ could be well represented (usually within a few percent) with model results corresponding to the simple phonon distribution

$$g_0(\omega) = (4\omega\epsilon_0'/\omega_0^3\sqrt{\pi}) \exp(-\omega^2/\omega_0^2) , \qquad (44)$$

provided ϵ_0' (the relaxation energy in the model) and ω_0 were treated as fitting parameters. A "Debye" model $g_1(\omega) = 3\epsilon_0'\omega/\omega_0^3\Theta(\omega_0-\omega)$ was also tried, but the *Ansatz* in Eq. (44) gave a better fit to our data, with the exception of Al, where g_1 gave a slightly better fit. For Al, however, the phonon effects are small. We therefore present our numerical results for $\langle \omega \rangle_\Gamma$ and Δ_Γ in the form of optimized model results corresponding to Eq. (44).

In Fig. 1 we show $\langle \omega \rangle_\Gamma / 2\epsilon_0'$ and $\Delta_\Gamma^2/\epsilon_0'^2$ as functions of Γ/ω_0, and in Table I we give ϵ_0' and ω_0 for Li, Na, Al, and K. The parameter ω_0 closely resembles the Debye energy, and ϵ_0' agrees well (within a few meV) with ϵ_0 (also shown in Table I) computed from the full $g(\omega)$. For reference, we also give the zero-temperature values of the number $\bar{n}(0) = \int g(\omega) d\omega$ of shakeup phonons, and the phonon broadening $\Delta(0)$ (standard deviation) without incomplete relaxation effects.

The lifetime-dependent part Δ_Γ of the phonon broadening is rather sharply peaked around $\Gamma = 0.68\omega_0$, corresponding to the maximum $\Delta_\Gamma = 1.05\epsilon_0'$ and $\langle\omega\rangle_\Gamma = -1.31\epsilon_0'$. For the alkali metals ϵ_0' is larger than the phonon broadening in absorption, $\Delta(0)$, at $T=0$ (see Table I), and when $\Gamma \sim \omega_0$ the effects of incomplete phonon relaxation should be large enough to show up also at room temperature. For Al, both $\Delta(0)$ and ϵ_0' are small. When $\Gamma \gtrsim 3\omega_0$, Δ_Γ is small compared to $\Delta(0)$, and the phonon effects in emission are then adequately described by the limiting case $\Gamma \to \infty$, where the incomplete relaxation of the phonons causes a quenching of the Stokes shift, but no additional broadening.

In Table II we have collected results on core-level widths from experimental soft-x-ray absorption (SXA), soft-x-ray emission (SXE), and x-ray photoemission (XPS) spectra involving the uppermost core level. We also give theoretical estimates of the phonon broadening in emission and absorption. Our key parameter Γ is not accurately known for these levels, but experimental estimates[1, 25, 26] indicate that the lifetime broadening Γ is somewhere in the range 5–50 meV, which covers the interesting case $\Gamma \simeq \omega_0$. For SXA and SXE, the listed experimental FWHM values were estimated from the edge width W (10–90%) by assuming a Gaussian line shape and by quadratically subtracting the Fermi broadening, with the exception of the absorption data for Li, where we quote the analysis in Ref. 25. The core-level binding energy is also listed and corresponds to the maximum in XPS and the 50% point of the SXA or SXE edge.

The agreement between the experimental SXA and XPS results is very good, but until very recently there was a considerable spread in the available SXE data, in particular for Li. Experimentally as well as theoretically, SXE is not as clear cut as SXA, and the experimental emission edges may depend on, e.g., the x-ray takeoff angle and the energy of the incident particles because of self-absorption.[27] The incident radiation may also cause structural disorder, and the temperature is not always accurately known. Self-absorption usually tends to sharpen the edge, and the problems are most severe when the absorption and emission edges overlap, as they do when incomplete relaxation is important.

After this article was initially submitted for publication, however, very accurate data were presented by Callcott and Arakawa[28,29] and by Crisp.[30] The remaining part of this section has been rewritten (July 1977) to incorporate a full comparison between these new data and our theory. There has also appeared a paper by Mahan[31] in which some of our results are independently obtained.

It is seen in Table II that the theoretical phonon broadening in absorption[11] agrees well with experiment for Na, Al, and K. For Li, however, the experimental absorption broadening is about 50% larger than the theoretical value at low T, and the discrepancy increases slightly with temperature. Equations (34) and (38) show that the SXA broadening $[\Delta(T)]$ is proportional to the core-hole coupling strength, while the "unrelaxed" part (Δ_Γ) of the SXE broadening is proportional to the second power of the coupling strength and thus more sensitive to errors in $g(\omega)$. In order to make a comparison possible between the present theory and experiment also for Li, we have chosen to rescale the calculated values[11] of B_n in Eq. (21) to give the experimental phonon broadening in absorption at low Γ.[25] The rescaled broadenings for emission and absorption do not overlap at zero temperature in the relaxed limit, which is a necessary and model-independent constraint. The values of ϵ_0', $\bar{n}(0)$, ϵ_0, and $\Delta(0)$ corresponding to the rescaled, semiempirical $g(\omega)$ are given in the second line in Table I. The theoretical results for Li discussed in the following are based on the semiempirical $g(\omega)$.

The actual shape of the total core-level broadening $C(\omega, \Gamma)$ in emission can be obtained from Eq. (19). $C(\omega, \Gamma)$ may be considered as a convolution of the Γ-independent broadening $D(\omega, 0)$ in Eq. (32) with an additional lifetime-dependent part

$$C_1(\omega, \Gamma) = \int_0^\infty dt\, dt' \exp\{2i[f_2(t) - f_2(t')] - i\omega(t-t') - \tfrac{1}{2}\Gamma(t+t')\} ,$$

containing all effects of incomplete phonon relaxation. In the line-shape calculations described below, we obtained $f(t)$ by an integration over the Brillouin zone, and a Gaussian mesh was used in the integration with respect to t and t'.

In Fig. 2 we show the relaxed part $D(\omega, 0)$ for Li and Na at three different temperatures, $T = 1$, 80, and 300 K. At $T = 1$ K, the thermal contribution to $D(\omega, 0)$ above the no-phonon line is too small to be seen in the plot, and the broadening is somewhat asymmetric. The asymmetry decreases with increasing temperature, and at room temperature $D(\omega, 0)$ is indistinguishable from a Gaussian. Al-

TABLE II. Experimental and theoretical estimates of core-level widths. The experimental data are extracted from x-ray phtoemission (XPS), soft-x-ray absorption (SXA), and soft-x-ray emission (SXE) spectra. The emission and absorption edge widths W (10-90%) and the core-level binding energy E relative to the Fermi energy are also given. The experimental FWHM widths include both phonon and lifetime broadening, unless stated otherwise. Energies in eV.

	Core		XPS		SXA			SXE		
Element	level	T (K)	E	FWHM	E	FWHM	W	E	FWHM	W
Li	K	4			54.9[a]	0.18[a,b]				
						0.12[c]				
Li	K	80	54.9[d]	0.22[d]	54.9[e]	0.21[b,e]	0.23[e]	54.70[f]	0.64[f]	0.70[f]
								54.72[g]	0.58[g]	0.63[g]
						0.12[c]			≤0.67[h]	
Li	K	300	54.9[d]	0.32[d]	55.0[a]	0.33[a,b]		54.73[g]	0.56[g]	0.61[g]
						0.18[c]				
Na	L_3	80			30.7[i]	0.05[i]	0.07[i]	30.56[f]	0.12[f]	0.14[f]
								30.55[j]	0.11[j]	0.12[j]
						0.08[c]			≤0.22[h]	
Na	L_3	300	30.5[k]	0.16[k]		0.16[i]	0.21[i]	30.60[j]	0.08[j]	0.13[j]
								30.58[l]	0.14[l]	0.19[l]
						0.15[c]			≤0.25[h]	
Al	L_3	80			72.72[m]	0.03[m]	0.05[m]	72.79[f]	0.06[f]	
Al	L_3	300	72.6[k]	0.05[k]				72.74[n]		
				0.06[c]		0.06[c]			≤0.07[h]	
K	M_3	80			18.35[o]	0.05[o]	0.06[o]	18.32[f]	0.12[f]	0.14[f]
						0.08[c]			≤0.22[h]	
K	M_3	300						18.3[p]	0.11[p]	0.17[p]
						0.15[c]			≤0.25[h]	

[a] Kunz *et al.* (Ref. 32). E includes the correction +0.16 eV from Kunz (Ref. 33).

[b] Phonon broadening according to the analysis by Baer *et al.* (Ref. 25). Lifetime broadening is not included.

[c] Theory; Hedin and Rosengren (Ref. 11).

[d] Baer *et al.* (Ref. 25). The quoted FWHM values are extracted by Citrin *et al.* (Ref. 26), and do not include lifetime effects. A correction has been made for recoil broadening using the theory by Flynn (Ref. 34).

[e] Petersen (Ref. 35).

[f] Crisp (Ref. 30). The width for Al is corrected for an instrumental resolution of 0.10 eV.

[g] Callcott and Arakawa (Ref. 28).

[h] Maximal broadening according to the present theory. A semiempirical core-hole coupling is used for Li.

[i] Petersen (Ref. 36).

[j] Callcott and Arakawa (Ref. 29).

[k] Citrin *et al.* (Ref. 26). The FWHM values do not include lifetime and recoil broadening.

[l] Crisp and Williams (Ref. 37).

[m] Kunz *et al.* (Ref. 38).

[n] Neddermeyer and Wiech (Ref. 39).

[o] Ishii *et al.* (Ref. 40).

[p] Norris (Ref. 41).

ready at zero temperature the strength $e^{-\bar{n}(T)}$ of the no-phonon line is negligible (see Table I), and one obtains with good accuracy a FWHM of $2.35\Delta(T)$. The absence of structure in $D(\omega, 0)$ is due to the high number of shakeup phonons and is no artifact of poor numerical convergence. The convergence in the Brillouin-zone integration was described above, and the number of mesh points in the resulting t integration was increased until full numerical convergence was achieved.

Figure 3 shows the total emission broadening for Li at 80 K and several values of Γ in the range 12–40 meV. The relaxed portion is represented by a Gaussian of the appropriate width and center-

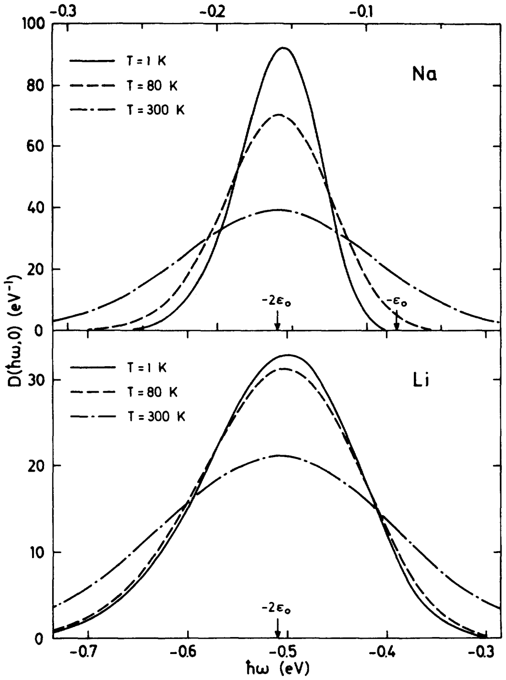

FIG. 2. Relaxed part $D(\hbar\omega, 0)$ of the phonon broadening in emission for Li and Na for $T = 1$, 80, and 300 K. The no-phonon line appears at the energy $-\epsilon_0$ and has a relative strength $e^{-\bar{n}(T)}$. The values of $\bar{n}$ for Li are 14, 21, and 62 for $T = 1$, 80, and 300 K, respectively. The corresponding values for Na are 11, 32, and 115. The broadening for Li is obtained from a semiempirical core-hole coupling as described in the text. The absorption broadening is the mirror image of $D(\hbar\omega, 0)$ in the no-phonon line.

ed at $\omega = -2\epsilon_0$, and the lifetime-dependent part C_1 is obtained by numerical integration. For comparison we also give the absorption broadening, represented by a convolution of a Gaussian and a Lorentzian and centered at $\omega = 0$. When $\Gamma \sim \omega_0$, the emission broadening for Li has two peaks. The upper peak is located $\sim 2\epsilon_0$ above the lower one and originates from reabsorbed shakeup phonons from the excitation step. The semiempirical core-hole coupling for Li as measured by $\bar{n}(0) = \int g(\omega) d\omega$ is quite large, and $\Delta(T)$ depends only weakly on T, since the Debye temperature is high (see Table I). This makes Δ_Γ much larger than $\Delta(T)$ when $\Gamma \sim \omega_0$ at all reasonable temperatures, and the emission broadening is then dominated by incomplete relaxation effects.

For Li, the emission edge width W (90–10%) and the 50% point E give a somewhat crude description of the emission broadening, since this is not at all Gaussian (Fig. 3). However, the great difference in edge width in emission and absorption (Table II) suggests that effects of incomplete phonon relaxation are present in the Li emission spectrum, and there is also evidence that the SXE and SXA edges overlap.[29]

A more accurate method for extracting Stokes shifts and broadenings from experimental data consists of convoluting a theoretical transition probability with the relevant broadenings and then comparing with experimental results. This is done in Fig. 4. The experimental emission and absorption curves were obtained by Callcott and Arakawa[29] using the same spectrometer. The position of the emission edge relative to the absorption edge should thus be unaffected by possible calibration errors.

The theoretical curves were calculated by first evaluating the electronic part corresponding to the length formula

$$\Lambda_v(\epsilon) \propto \sum_{\mathrm{BZ}} |\langle \vec{\mathrm{k}} | r_z | c \rangle|^2 \delta(\epsilon_{\vec{\mathrm{k}}} - \epsilon_c - \omega) .$$

We then broadened with our phonon and lifetime function and also with the Fermi function and finally we multiplied the emission spectrum with $(\omega/\omega_t)^3$ and the absorption spectrum with ω/ω_t. Here ω is the actually measured photon energy, and ω_t is the threshold energy (54.9 eV). Thus Fig. 4 exhibits a close similarity to the theoretical

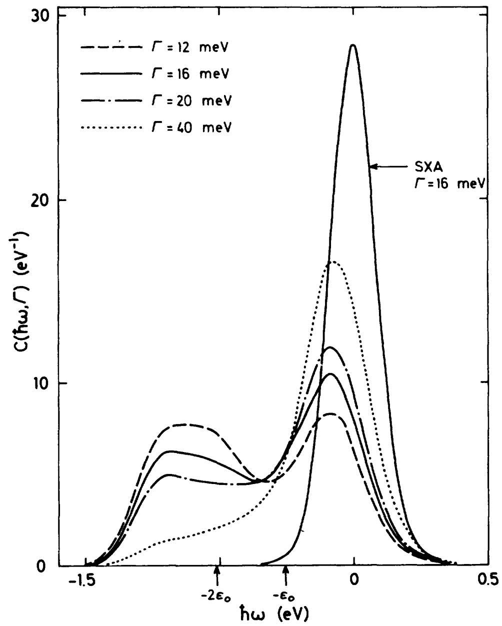

FIG. 3. Emission broadening, including phonon and lifetime effects, for Li at 80 K and four different values of the core-hole lifetime. The absorption broadening for $\Gamma = 16$ meV is also shown. The core-hole coupling is scaled to give the experimental broadening in absorption at low T.

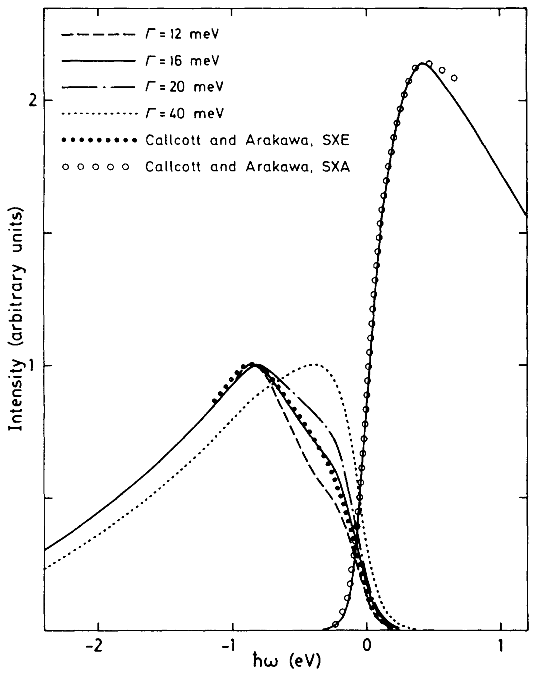

FIG. 4. Calculated x-ray emission and absorption edges for Li at 80 K and four different values of the core-hole lifetime. Experimental absorption and emission spectra (85 K), recorded with the same spectrometer, from Callcott and Arakawa (Ref. 29) are also given. The theoretical SXE-SXA edges for $\Gamma = 16$ meV have a Stokes shift of 320 meV.

electronic transition density $\Lambda_v(\epsilon)$. This quantity was calculated by von Barth and Grossmann[42] using self-consistent wave functions.

Many-electron effects such as, e.g., those proposed by Mahan[43] and Nozières and DeDominicis[44] are accounted for in the present theory by the term V_v in Eq. (2). Experimentally, inelastic electron scattering[45] shows that these effects are small for Li. Girvin and Hopfield[46] have extended the theory in Refs. 43 and 44 to include spin-dependent effects. Their numerical evaluation, however, was in our opinion oversimplified. We have made accurate calculations[47] of the Girvin-Hopfield expressions[46] along similar lines as in Ref. 20. We find that the x-ray edge exponents corresponding to the theory in Refs. 43, 44, and 46 are close to zero, while the corresponding exponent for XPS is increased. Thus, both experimentally and theoretically it seems clear that the singular edge effects are small for Li, and we have made no attempts to include them in the present work.

The theoretical absorption spectrum depends only weakly on Γ. It is therefore sufficient to give only our $\Gamma = 16$ meV curve in Fig. 4. The theoretical emission spectrum, however, is very sensitive to the core-hole lifetime, and both the position of the edge, i.e., the Stokes shift, and the edge shape change considerably with changes in Γ. For $\Gamma = 16$ meV we obtain a very good agreement with both the experimental Stokes shift[29] and the edge shape.[28-30] For this value of Γ the theoretical SXE-SXA edges have a Stokes shift of 320 meV, which may be compared to the value $2\epsilon_0 = 510$ meV corresponding to complete relaxation. An interesting feature of the $\Gamma = 16$ meV and $\Gamma = 20$ meV curves is the shoulder on the emission edge. Experimentally, this shoulder was first observed by Skinner,[1] and later by Crisp and coworkers[48, 49] but not by other groups,[50, 51] and it was suspected that the shoulder might be an experimental artifact. After the original submittance of the present article, however, the edge shape observed in Refs. 1, 48, and 49 has been experimentally confirmed.[28-30]

We have also calculated emission edges for Na and K using the full emission broadening. We find that the edge width W at 80 K agrees within 10% or better with results obtained from a Gaussian broadening with a width $[\Delta^2(T) + \Delta_\Gamma^2]^{1/2}$, and the 50% point approximates the Stokes shift within 15 meV. The accuracy is better at room temperature or when Δ_Γ is small. These errors are of the same order as present experimental uncertainties, and we shall use the moment analysis in Fig. 1 and Table I for interpreting the data for the other metals studied in this paper.

We now return to Table II. For Na, the experimental emission broadening[29, 30] at 80 K exceeds the absorption broadening,[36] in accordance with the present theory. The difference in edge widths indicates that $2.35\Delta_\Gamma \simeq 100$ meV, which according to Fig. 1 and Table I corresponds to $\Gamma \simeq 20$ meV or $\Gamma < 1$ meV. The lower value is much smaller than other estimates presented so far and can probably be ruled out. The above value of Δ_Γ may be uncertain owing to the difficulties in extracting small broadenings from experimental data. Using the low-T data above and experimental or theoretical values for $\Delta(T)$, it is found that the emission and absorption widths should be of almost the same width at room temperature (the difference is ~30 meV). The experimental emission edge is actually somewhat sharper than the absorption edge at room temperature, possibly because of self-absorption.

For Al, the SXA[38] and SXE[39] edges coincide within 20 meV, which is consistent with a small lattice relaxation energy ($\epsilon_0 = 13$ meV).[11] The effects of incomplete phonon relaxation are probably too small to be seen experimentally, even at low temperatures.

The data for K, finally, are similar to those for Na. The low-temperature data for emission and absorption indicate that incomplete phonon relaxation gives a contribution with a FWHM of $2.53\Delta_\Gamma \simeq 100$ meV to the emission edge width. This would correspond to $\Gamma \simeq 14$ meV and a Stokes shift of 25 meV, or $\Gamma < 0.5$ meV. As for Na, the lower value of Γ is less likely. The effects of incomplete relaxation are probably too small to be seen at room temperature.

In summary, we find strong evidence that incomplete phonon relaxation contributes significantly to x-ray emission edge width in Li. There is also indication that the effect is present in the emission spectra of Na and K at low T, but the effect should be very small for Al. It is also clear that significant effects of incomplete phonon relaxation imply that *the temperature dependence of the edge width is weaker in emission that in absorption,* since the two contributions Δ_Γ and $\Delta(T)$ should be added quadratically. This prediction is supported by the new data cited in Table II.

The main uncertainties in the present work are the same as in Ref. 11, and are caused by the harmonic pseudopotential approximation[52] for the phonon dynamics and the use of Eq. (43) for calculating the core-electron binding energy. We think that the above approximations should be reasonably accurate for Na, Al, and K, and thus when $\Gamma \simeq \omega_0$ the present calculation should offer a possibility of determining Γ from emission data, since the lifetime-dependent part Δ_Γ of the phonon broadening is then rapidly varying with Γ.

For Li, the pseudopotential approach is not so well justified owing to the absence of p states in the core, and the nonlinear part of the core-level polarization energy is larger ($\simeq 1$ eV).[20] Anharmonicity may also be important because of the low nuclear mass. No *a priori* calculation presented so far can quantitatively account for the observed phonon broadening in absorption, and further theoretical work is evidently needed. In this work we rescaled the core-hole coupling with 50% in the calculation of the emission and absorption edges in Fig. 4, in order to get agreement for absorption. We could then obtain a detailed agreement with *both* the experimental Stokes shift, which we found to be 320 meV, and the line shape for $\Gamma = 16$ meV. In view of the good agreement we believe that the lifetime width of the 1s level cannot be very far from the optimum value $\Gamma = 16$ meV. At any rate, the qualitative features of incomplete phonon relaxation are not restricted to the model used in the numerical part of this work. In particular, the phonon broadenings for emission and for absorption can *only* overlap appreciably when the core-hole lifetime is comparable or shorter than the phonon relaxation time, and the emission edge width exceeds the width of the absorption edge only when these two times are of comparable magnitude.

V. SUMMARY AND CONCLUSIONS

In this paper we have applied the theory of deep-level emission phenomena to the phonon broadening in x-ray emission. We have outlined the basic theory in Sec. II, and the treatment of lifetime effects and core-hole relaxation in emission spectroscopies has been given its due attention. The phonons have been introduced within the Born-Oppenheimer approximation without invoking any specific model for the phonon dynamics. However, no valence-electron–phonon interaction has been included. Within these approximations the phonon part of the problem separates out, and the basic correlation function that describes the total process factorizes in an electronic part and a phonon part.

The phonon part of the problem has been evaluated exactly for harmonic phonons with the usual linear core-hole coupling, and explicit expressions for the shape and the first frequency moments of the phonon broadening in emission have been obtained (Sec. III). The phonon broadening has has been discussed for different values of the lifetime width Γ. We have shown that the phonon broadening in emission reflects a local equilibrium for small Γ, and the statistical fluctuations in the instantaneous nuclear positions, in accordance with a semiclassical Frank-Condon picture, in the other limit $\Gamma \to \infty$. In both cases the phonons give the same contribution to the core-level width, the main difference being that no Stokes shift was present in the limit $\Gamma \to \infty$. In the intermediate range, when Γ is of the same order as the Debye energy, the shakeup phonons from the initial excitation give a temperature-independent contribution to the phonon broadening in emission.

The phonon response to the total process of excitation and subsequent emission has been thoroughly discussed, and we have explicitly shown that the phonons are unaffected by the deep-level process in the limit $\Gamma \to \infty$. This is the physical explanation of why the phonon broadening in emission is the same as in absorption in this limit. We have also discussed the emission at threshold excitation.

Numerical evaluations have been carried out for four simple metals. For these metals the lifetime-dependent part Δ_Γ of the phonon broadening and the Stokes shift as functions of Γ can be represented by the same two curves, after a suitable rescaling (Sec. IV). We have found that incomplete phonon relaxation can contribute significantly to the emission edges for Li, Na, and K, while the phonon effects for Al are small. Available emission data have also been discussed, and we argue that with the exception of Li the uncertainty in the data may still be too large to allow definite conclusions about the size of the incomplete relaxation effects. However, we have found strong evidence that these effects are present for Li, and possibly also for Na and K.

After a 50% rescaling of the core-hole coupling for Li to get agreement with the experimental phonon broadening in SXA at low temperatures we can account for both the observed Stokes shift and the edge width in emission, and we think that incomplete phonon relaxation is likely to be the explanation of the broad edge in the x-ray emission spectrum for Li.

We have discussed the main uncertainties involved in the calculation, and we conclude that the pseudopotential approximation used for calculating the phonon dynamics should provide a quantitative description for Na, Al, and K, while the accuracy for Li is more uncertain. However, as long as the phonons are reasonably well-defined elementary excitations in spite of anharmonicity and other effects outside the model used in Secs. III and IV, the phonon relaxation time will still be determined by the Debye frequency. Effects of incomplete phonon relaxation in the x-ray emission spectrum from Li therefore limit Γ to a narrow range, and the suggestions that Γ should be of the order 0.2–0.5 eV seem to be borne out.

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APPENDIX

In this appendix we show the equivalence between the limit in Eq. (11) and the assumption that local equilibrium near the core hole is eventually obtained. For simplicity we consider the case $T=0$.

Let $|\psi\rangle$ represent a state where the system is perturbed near the origin, and let S be an observable measuring a local property at the origin, such as, e.g., the charge density. $|\psi\rangle$ is in general not an eigenstate. The assumption that local equilibrium is obtained after a long time means that the expectation value of S tends to the ground-state value in the limit $t\to\infty$,

$$\langle \psi | S(t) | \psi\rangle / \langle \psi | \psi\rangle \to \langle 0 | S | 0\rangle ,$$

$|0\rangle$ being the ground state. The above limit applies when $|\psi\rangle$ is made up of eigenstates corresponding to the case when the core level is filled. In the other case, when $|\psi\rangle$ only contains states with empty core level, the lowest state $|0^*\rangle$ consistent with an empty core level plays a similar role as the ground state did in the first case, since H_0 does not allow the core hole to disappear. We then have

$$\langle \psi | S(t) | \psi\rangle \to \langle \psi | \psi\rangle \langle 0^* | S | 0^*\rangle \tag{A1}$$

when $t\to\infty$.

We now consider two states, $|\psi\rangle$ and $|\varphi\rangle$, of the above type made up by empty core-level states and apply Eq. (A1) to the linear combination $\alpha\,|\psi\rangle + \beta\,|\varphi\rangle$. Identification of the coefficients for α and β yields the relation

$$\langle \psi | S(t) | \varphi\rangle \to \langle \psi | \varphi\rangle \langle 0^* | S | 0^*\rangle \tag{A2}$$

when $t\to\infty$. Choose now

$$|\varphi\rangle = T_A(\vec{p}, t_4) b(t_4) |0\rangle ,$$

$$|\psi\rangle = T_A(\vec{p}, t_1) b(t_1) |0\rangle ,$$

and

$$S \equiv S(0) = T_r(\vec{q}\lambda, t_2 - t) b(t_2 - t) \times b^\dagger(t_3 - t) T_r^\dagger(\vec{q}\lambda, t_3 - t) .$$

Here t should be chosen in the vicinity of t_2 and t_3; we may take, e.g., $t=\frac{1}{2}(t_2+t_3)$. Since the transition operators $T_r(\vec{q}\lambda, \tau)$ and $T_A(\vec{p}, \tau)$, for finite values of τ, only probe the system in the vicinity of the atom that is being excited, we can apply Eq. (A2), and the limit in Eq. (11) follows.

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