Phonon Broadening of Deep Excitations in Metals*

C. P. Flynn
Physics Department and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

(Received 19 July 1976)

A novel and widely applicable treatment of phonon creation by core excitations in metals and alloys is used to examine results reported in recent Letters.

Several recent Letters discuss evidence for phonon broadening of the x-ray lines shapes for core levels in metals.[1-4] In particular, appropriate temperature dependences of profiles have been detected.[2,4] Unfortunately, the experimental situation is complicated for metals by a number of additive broadening and distorting processes.[4] A determined effort is therefore needed to confront theory with experiment even for the simplest metals. Quantitative first-principles calculations of the core hole coupling to the lattice are also lacking, other than model results for alkali metals.[1,5,6] Thus, neither theory nor experiment yet provides a framework within which an informed discussion of the general occurrence and size of phonon effects in metals can proceed. In this Comment, we present a new treatment that resolves the difficulty. Our procedure can be applied with ease to simple metals, transition metals, and even impurity spectra in alloys. Phonon broadening is found to vary by two orders of magnitude among the 31 pure metals treated here but rarely exceeds 0.25 eV at room temperature. The broadening also depends on the particular x-ray process in question. Experimental data reported in recent Letters are discussed in the light of these new facts.

Consider an electronic process confined to one core of a solid. Suppose that the process imparts momentum $\vec{p}_0$ to the active core with mass M_0 and position $\vec{r}_0$ and has no other influence on the motion of the remaining N cores of mass M_μ and positions $\vec{r}_\mu$, where $\mu = 1, 2, \ldots, N$. The normalized probability that the process induces a transition from state Φ_n of the lattice modes in the ground electronic configuration to vibrational state $\Phi_{n'}'$ of the solid in the excited electronic configuration is just[7]

$$W_{nn'} = |\langle \Phi_n | \exp(i\vec{p}_0 \cdot \vec{r}_0/\hbar) | \Phi_{n'}' \rangle|^2. \tag{1}$$

Core hole lifetimes and the accessible x-ray resolution both limit significant spectral features to the energy range ($\gtrsim 0.05$ eV) of *multi*phonon processes. Moreover, local electronic states couple to few atoms and hence many phonons. Under these circumstances[8] the probability $f(E)$ that energy E is absorbed by phonons reduces to a displaced Gaussian:

$$f(E) = \langle \textstyle\sum_{n'} W_{nn'} \delta(E - E_{n'} - E_n) \rangle_n \to (2\pi F_2')^{-1/2} \exp[-(E - F_1)^2/2F_2'], \tag{2}$$

with the $F_m = \langle E^m f(E) \rangle$ moments of f and $F_2' = F_2 - F_1^2$.

For the ground-state lattice wave functions we take products of oscillator states, $\varphi_\nu(\alpha_q s_q)$, in excitations levels ν_q, with $\alpha_q^2 = \omega_q/\hbar$. Here, the $3(N+1)$ normal-mode vectors s_q diagonalize the potential energy $V(\vec{s})$ in the space of $N+1$ mass-weighted coordinates $\vec{s}_\mu = \vec{r}_\mu M_\mu^{1/2}$, and the ω_q are the associated mode frequencies. The lattice states of the excited configuration for linear coupling are[8] products of *displaced* oscillator functions $\varphi_{\nu'}[\alpha_q(s_q - \epsilon_q)]$. When $M_0^{-1/2}\vec{p}_0$ is now resolved into mass-weighted component momenta σ_q, so that $\vec{p}_0 \cdot \vec{r}_0 = \sum_q \sigma_q s_q$, the matrix elements in Eq. (1) factor into products of single-mode matrix elements

$$w_{\nu\nu'} = \left| \langle \varphi_\nu(\alpha_q s_q) | \exp(i\sigma_q s_q/\hbar) | \varphi_{\nu'}[\alpha_q(s_q - \epsilon_q)] \rangle \right|^2. \tag{3}$$

A center weakly coupled to many lattice modes has ϵ_q, σ_q small; then $w_{\nu\nu'} = \delta_{\nu\nu'}$, apart from small terms with $\nu' = \nu \pm 1$ of second order in ϵ_q *or* σ_q (the two types of terms *cannot* interfere in lattices possessing inversion symmetry). Using the approximation $\exp(i\sigma s/\hbar) \simeq 1 + i\sigma s/\hbar$ and addition formulas for normalized oscillator states,[9] one can now write down the required moments directly from well-known results[8] for $\sigma = 0$ and the explicit independence of terms in σ and ϵ. Thus,

$$F_1 = \tfrac{1}{2} \textstyle\sum_q \zeta_q^2; \quad F_2' = \sum_q \zeta_q^2 E_q, \tag{4}$$

with

$$\zeta_q^2 = |\sigma_q|^2 + \omega_q^2 |\epsilon_q|^2, \tag{5}$$

and

$$E_q = (\hbar\omega_q/2)\coth(\hbar\omega_q/2kT). \tag{6}$$

Our aim is to apply these general (linear-coupling) results to metals and alloys.

To obtain σ and ϵ, and hence F_2', we first note an exact result for σ at high temperatures, when $E_q \to kT$ and $\sum_q \sigma_q^2 kT \to p_0^2 kT/M_0$ exactly. Approximations are necessary in other cases. Plane-wave phonons give

$$\sigma_q = \vec{e}_q \cdot \vec{p}_0 / [M_0(N+1)]^{1/2}, \tag{7}$$

with $\vec{e}_q$ the polarization vector. This result is fully appropriate only for host excitations but will also serve well for impurities that do not greatly perturb the host dynamical matrix.

The normal-mode displacements ϵ_q are driven by chemical forces and can be approximated by a simple method. The main idea[10] is that an atom excited by promotion of one deep core level to the lowest available valence orbital resembles in size, valence, ionization potential, orbital structure, etc., the *un*excited atom on its right in the periodic table. For example, $2p^5 3s^2$ Na* resembles $2p^6 3s^2$ Mg, and $3p^5 3d^{10} 4s$ Ni* resembles $3p^6 3d^{10} 4s$ Cu. In each case the extra core orbital and nuclear charge of the heavier atom sum to a pseudopotential confined to a core region from which the chemically active valence states are largely excluded. This is an approximation whose validity obviously improves with increasing depth of the core hole. We neglect the weak perturbation imposed on the valence chemistry by the modified pseudopotential and assert that the ϵ_q take values appropriate to the dilute alloy in which the excited center is replaced by the ground state of its right-hand neighbor in the periodic table. The advantage of this scheme is that the required results are often available in the literature from lattice-parameter measurements on alloys.

Suppose that the center causes displacements $\vec{u}_\mu$ of the host atoms μ in this substitute alloy system. Then by definition $\epsilon_q = \sum_\mu \vec{u}_\mu \cdot \vec{s}_{q\mu}/M_\mu^{1/2}$, with $\vec{s}_{q\mu}$ the displacement of μ associated with the unit vector along s_q. A simple procedure giving direct contact with experiment is to use the strain field,

$$\vec{u}_\mu = \frac{\Omega\Delta\vec{r}_\mu}{12\pi r_\mu^3}, \quad \Delta = \frac{1+\sigma_\mathrm{P}}{1-\sigma_\mathrm{P}}\left(\frac{\delta V}{\Omega}\right), \tag{8}$$

of elasticity theory, with Ω the molecular volume, σ_P Poisson's ratio, and δV the volume change of the solid per center. Then, with $M_\mu = M$, $\mu \neq 0$,

$$\epsilon_q = (i\vec{q} \cdot \vec{e}_q \Delta/3q^2)[M/(N+1)]^{1/2}. \tag{9}$$

Finally, to evaluate the summations in Eqs. (4) we represent the dispersion curve for longitudinal phonons by $\omega_q = (2q_\mathrm{D}c/\pi)\sin(\pi q/2q_\mathrm{D})$, to find the desired results:

$$F_2' = 2kTF_1; \quad F_1 = \frac{P_0^2}{2M_0} + \frac{Mc^2\Delta^2}{3\pi^2} \tag{10}$$

at high temperature, where F_1 is temperature-independent; and at low temperature

$$F_2' = \frac{P_0^2 E_0}{M_0} + \frac{16Mc^3\hbar q_\mathrm{D}\Delta^2}{9\pi^4}. \tag{11}$$

In these equations q_D is the Debye radius, c is the longitudinal sound velocity, and E_0 is the zero-point energy. Values of F_2' at intermediate temperatures may be obtained directly from Eq. (4) (F_2' tracks closely with the vibrational energy).

Table I presents predicted phonon widths at room temperature for x-ray absorption and emission in 31 pure metals. For these processes $p_0 \simeq 0$. Values are given for $W = 2(2F_2' \ln 2)^{1/2} \simeq 2.355(F_2')^{1/2}$, the Gaussian width at half its maximum height. Tabulated values of $(1-\sigma)/(1+\sigma)$[11] and c[12] were used with $\delta V/\Omega$ obtained from Pearson's book,[13] or from Vegard's law (i.e., additivi-

TABLE I. Widths (in meV) of phonon broadening of x-ray edges (W) and XPS lines using Al *Kα* (W_Al) and Cu *Kα* (W_Cu) radiation, according to Eq. (10) with $T = 300$ K. Small corrections for $T \sim \theta_\mathrm{D}$ have been made for Li only.

	W	W_Al	W_Cu		W	W_Al	W_Cu
Ag	125	134	169	Nb	162	170	203
Al	93	133	247	Ni	57	86	165
Au	149	153	171	Pb[a]	32	47	88
Co	9	65	155	Pd	137	145	179
Cr	7	69	165	Pt	138	142	162
Cs[a]	141	147	176	Rb[a]	119	130	175
Cu	137	150	202	Re	94	101	128
Fe	6	66	159	Ru	4	49	118
Hg[a]	104	110	134	Sn	46	65	118
Ir	118	123	146	Ta	167	171	189
K[a]	130	152	230	Ti	205	217	267
Li[a]	210	288	517	Tl	58	68	101
Mg	169	197	294	V	27	74	168
Mo	96	108	155	W[a]	109	115	139
Na[a]	106	148	269	Zn[a]	161	174	227
				Zr	237	243	268

[a] Obtained using Vegard's law to find $\delta V/\Omega$.

ty of constituent molar volumes, as discussed, for example, in Ref. 13) when data were otherwise lacking. The calculated widths range from 4 meV (Ru) to 237 meV (Zr); very little broadening occurs for several transition metals where the size misfit between neighboring elements is small (this is the case for many rare-earths also). In the present approximation, the same phonon broadening occurs for all deep levels that have the same final valence configuration.

Widths for x-ray photoemission spectroscopy (XPS) processes induced by Al $K\alpha$ and Cu $K\alpha$ radiations, at about 1.5 and 9 keV, respectively, are given in Table I as values of $W_{\rm Al}$ and $W_{\rm Cu}$. The ionic recoil from the emitted photoelectron determines $\vec{p}_0$ in Eq. (10). For light elements the added effect is very significant even for Al $K\alpha$ radiation. In the case of Li, for example, σ and ϵ contribute almost equal terms (~ 0.2 eV each) to the final XPS width of 0.29 eV predicted here. Values of $W_{\rm Al}$ and $W_{\rm Cu}$ given in Table I are accurate only for shallow levels because the core excitation reduces the available recoil energy. For the 55-eV 1*s* level of Li, the correction to $W_{\rm Al} = 0.288$ eV is about 0.002 eV.

Experimental data for Li exhibit a broadening comparable with that predicted here. The room temperature XPS result $W_{A1} = 0.35 \pm 0.02$ eV[4] compares well with the value 0.29 eV in Table I. Analyses of electron scattering results[14] give $W = 0.38 \pm 0.02$ eV[14] and $W = 0.35$ eV[4] at room temperature, and an analysis[4] of photoyield data[2] gives $W = 0.33$ eV. These are to be compared with a predicted $W = 0.21$ eV (Table I) and a value $W = 0.29 \pm 0.02_5$ eV obtained by deconvoluting the predicted recoil broadening from the experimental XPS result quoted above. Data now becoming available[15] suggest that the predictions for Na are also satisfactory. Both theory and experiment[2-4,14] show that the broadening varies in approximate proportion to the vibrational energy of the metal.

TABLE II. Widths of some impurity x-ray edges.

Host	Core	T (K)	W (meV)
Fe	C	300	43
Ag	Ag	300	125
Ag	Cd	300	44
Ag	In	300	31
Ag	Sn	300	101
K	Xe	0	24
Rb	Xe	0	31
Cs	Xe	0	37

For *impurity* spectra we simply substitute the difference $\Delta_e - \Delta_g$ of excited- and ground-state size misfit factors for Δ in Eqs. (10). The exact result for σ at high temperature also still holds. A plane-wave approximation to σ, useful for lower temperatures, may be fairly satisfactory whenever the defect modes spread throughout the band. Other simple approximations are available for impurities with resonance or local modes sharply centered on particular frequencies.

Illustrative room-temperature predictions for alloys, presented in Table II, include an important interstitial solute (C in Fe) and a classic series of positive-valence solutes (Cd, In, Sn in Ag). The widths are uniformly of modest size. The last three rows of Table II report widths at He temperatures for rare gas impurities in alkali metals.[10] The widths ~0.03 eV are much too small to play a significant part in the unexplained rounding of threshold profiles on a scale ~1 eV observed in these interesting systems.

Figure 1 displays for 35 pure metals and alloys at $T = 300$ K the predicted distributions of widths W, $W_{\rm Al}$, and $W_{\rm Cu}$; it provides the first comprehensive view of phonon effects for deep levels in metals. For clarity, the figure shows the integrals

$$n(W) = \int_0^W \sum_i \delta(E - W_i)\, dE, \tag{12}$$

with the W_i individual widths. Differences apparent between the three distributions are probably real since the *excess* XPS broadening is predicted exactly at high temperature. The net uncertainty of a factor of ~2 in individual W_i still

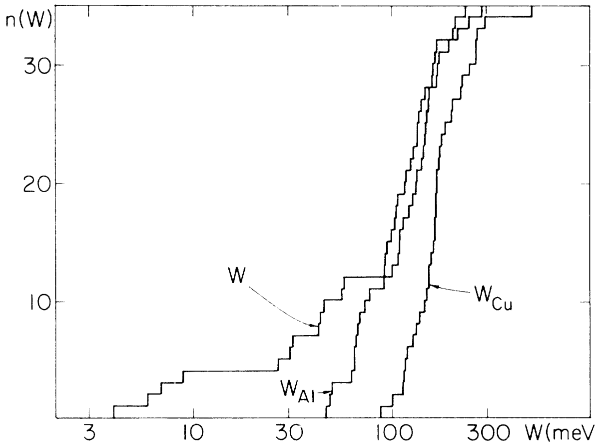

FIG. 1. Distribution of phonon widths for 35 pure metals and alloys at room temperature, i.e., $n(W)$ as defined in Eq. (12) versus W.

leaves the distributions adequately defined. A more precise analysis may eliminate some cases with W very small. It has been shown using lattice statics[16] that the elasticity result (10), which limits the present accuracy, yields strain energies correct within a factor 2 and hence values of the widths $(F_2')^{1/2}$ probably accurate to a factor of $\sim\sqrt{2}$.

We conclude from these results that the phonon broadening of x-ray processes in metals is generally weak. The predicted Li width, emphasized in this Comment, is in the largest 10%, and a better pure metal for study of phonon broadening is not likely to emerge. Impurities offer better possibilities. Halogens in alkali metals have $F_1 \simeq 1.5$ eV and $W \simeq 0.3$ eV at He temperature[17] (~0.8 eV at 300 K). A number of systems promising still larger widths are now being investigated in our laboratories.

Thanks are due to Professor J. D. Dow for stimulating discussions.

---

*Supported by National Science Foundation under Grant No. DMR-72-03026 and by the U. S. Office of Naval Research.

[1] J. D. Dow, J. E. Robinson, and T. R. Carver, Phys. Rev. Lett. 31, 759 (1973).

[2] C. Kunz, H. Petersen, and D. W. Lynch, Phys. Rev. Lett. 33, 1556 (1974).

[3] H. Petersen, Phys. Rev. Lett. 35, 1563 (1975).

[4] Y. Baer, P. H. Citrin, and G. K. Wertheim, Phys. Rev. Lett. 37, 49 (1976).

[5] B. Bergersen, T. McMullen, and J. P. Carbotte, Can. J. Phys. 49, 3155 (1971).

[6] A. J. McAlister, Phys. Rev. 166, 595 (1969).

[7] This is the familar Mössbauer result applied here to core processes; see H. Frauenfelder, *The Mössbauer Effect* (Benjamin, New York, 1963).

[8] See A. M. Stoneham, *Theory of Defects in Solids* (Oxford Univ. Press, Oxford, England, 1974).

[9] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), pp. 1642 and 1646.

[10] R. A. Tilton, D. J. Phelps, and C. P. Flynn, Phys. Rev. Lett. 32, 1006 (1974).

[11] K. Gschneidner, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1964), Vol. 16.

[12] G. Simmons and H. Wang, *Single Crystal Elastic Constants* (MIT Press, Cambridge, Mass., 1971).

[13] W. B. Pearson, *Handbook of Lattice Spacings* (Pergamon, New York, 1958).

[14] For Li, see J. J. Ritsko, S. E. Schnatterly, and P. C. Gibbons, Phys. Rev. B 10, 5017 (1974).

[15] H. Petersen, private communication.

[16] P. A. Flinn and A. A. Maradudin, Ann. Phys. (N.Y.) 18, 81 (1962).

[17] R. Avci and C. P. Flynn, Phys. Rev. Lett. 37, 864 (1976).