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The Mahan Soft-X-Ray Anomaly in Lithium: Relationship to the Knight Shift

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The Li soft-x-ray absorption-threshold shape is expressed in terms of the pressure-dependent Knight shift, using a one-electron model and accounting for the indirect interaction of the lattice with the 1*s* core, but neglecting the final-state interactions currently thought responsible for the anomalous shape.

In recent years, studies of "many-body effects" on the optical properties of metals have centered on the "x-ray anomalies" and their relationships to Mahan's model[1] of the final-state interaction. The primary prediction of the Mahan theory (in its current form[2-4]) is that the soft-x-ray absorption spectrum of a simple metal, $\epsilon_2(\omega)$, should exhibit an "anomalous" threshold behavior, corresponding to electronic transitions from a core level to a conduction-band state above the Fermi energy E_F:

$$\epsilon_2(\omega) \propto (\hbar\omega - E_F - E_{gap})^{-\alpha}\,\theta(\hbar\omega - E_F - E_{gap}).$$

Here the zero of energy is taken at the center of the core band, E_{gap} is the energy of the bottom of the conduction band, and $\theta(x)$ is the unit step function. The Mahan exponent α can be expressed in terms of the partial-wave phase shifts at the Fermi energy,[5] and may be either positive or negative.

The three principal experimental data cited as support for the Mahan theory are spikes in the soft-x-ray (30–60 eV) absorption spectra of metallic Na and Mg ($\alpha > 0$) and a rounded soft-x-ray absorption threshold in Li ($\alpha < 0$).[6] The spectra of a number of other materials (e.g., Al, Be) exhibit structures tentatively but ambiguously assigned to either "Mahan anomalies" or "band-structure effects."

The observed rounded threshold of Li [Fig. 1(b)] is currently thought to be conclusive evidence for the validity of the Mahan theory,[4] which predicts rounding whenever α is negative; Ausman and Glick[4] calculate $\alpha = -0.104$ for Li. However, this many-electron explanation seems deficient in at least three ways. First, the Mahan threshold shape $(\hbar\omega - E_F - E_{gap})^{-\alpha}$, as calculated using the Ausman-Glick exponent, disagrees qualitatively with the data [Fig. 1(b)]. Second, the observed Li emission[7,8] [circles in Fig. 1(b)] and absorption spectra overlap throughout an energy interval approximately equal to the edge breadth. In contrast, the many-electron theory gives mirror-image absorption and emission edges, which do not overlap but meet in a cusp.[5] Third, in calculating α, Ausman and Glick take the excited electron's angular momentum to be a good quantum number.[9] Band-structure effects and electron-phonon interactions combine to destroy both rotational and inversion symmetry, allowing

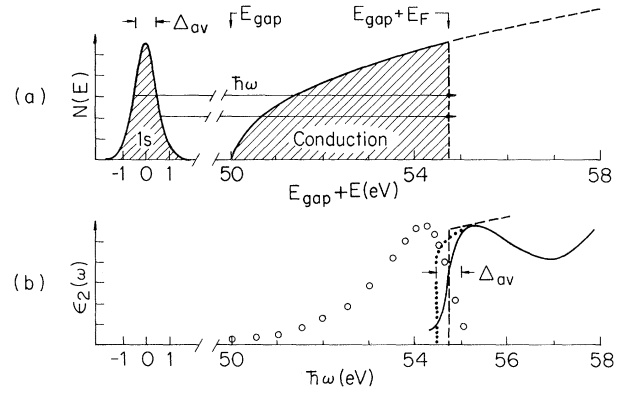

FIG. 1. (a) Sketch of densities of states $N(E)$, in arbitrary units, versus energy E, in eV, for Li including a filled (shaded) $1s$ core band of width Δ_{av} and the filled (shaded) conduction band. Optical transitions of energy $\hbar\omega$ from the core band to states above the Fermi surface are indicated by heavy lines. (b) Optical absorption spectra $\epsilon_2(\omega)$, in various (different) arbitrary units, versus photon energy $\hbar\omega$ in eV. Only the *shapes* of the curves $\epsilon_2(\omega)$ are relevant. Solid line, measurement by Kunz *et al.* (Ref. 6); dashed line, constant-matrix-element, narrow-core-band one-electron theory, with $E_{gap}+E_F$ chosen at the center of the observed edge (presumed phonon-broadened); dotted line, Mahan theory, for $\alpha=-0.104$, with $E_{gap}+E_F$ chosen to coincide with the threshold of the observed edge (presumed rounded by the Mahan effect); circles, emission data, not $\epsilon_2(\omega)$, of Sagawa (Ref. 7). Note the overlap of emission and absorption data.

transitions to s-wave conduction states; thus, the absorption at threshold should be infinite ($\alpha>0$), not zero ($\alpha<0$).[10,11] In this Letter, we present a *one-electron* theory that attributes the Li threshold behavior to a simulated $1s$ bandwidth caused by the *indirect* interaction of the $1s$ core state with the lattice.

The x-ray absorption process creates a hole in a core level and an electron above the Fermi surface [Fig. 1(a)]. *If the hole band is narrow, since the Fermi surface is sharp, one-electron theory predicts an abrupt threshold*

$$\epsilon_2^0(\omega)\propto A(\hbar\omega-E_{gap})\,\theta(\hbar\omega-E_F-E_{gap}), \qquad (1)$$

where $A(E_F)$ is finite. However, *if the core band has significant width* Δ_{av}, *the image of the Fermi surface is blurred over a spectral region of width* Δ_{av} [Fig. 1(b)], giving a broad absorption edge, with a shape expressible as a convolution[12] of ϵ_2^0 [Eq. (1)] with the core-band density of states N_{core}:

$$\epsilon_2(\omega)\propto\int N_{core}(\Delta)\,\epsilon_2^0(\omega-\Delta)\,d\Delta.$$

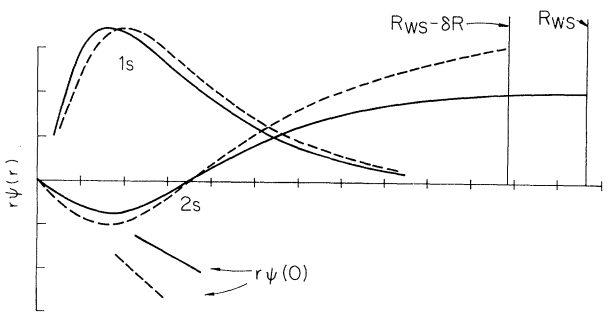

FIG. 2. Sketch of radial $1s$ and $2s$ wave functions $r\psi(r)$ versus r in Wigner-Seitz cells of radii R_{WS} (solid) and $R_{WS}-\delta R$ (dashed). Note that $\psi(0)$, the slope of the $r\psi(0)$ line, increases as the cell is compressed. The Wigner-Seitz boundary condition for $r\psi(r)$ is $(r\psi)'=\psi(R_{WS})$.

The experimental data for Li, both for emission and for absorption [Fig. 1(b)], are consistent with this picture, provided Δ_{av} is approximately 0.5 eV. Thus there remains only the question, "*Why is the 1s core level 0.5 eV wide for Li?*" Tight-binding band theory predicts negligible width (≈ 2 meV); the *direct* interaction of the $1s$ level with the lattice vibrations likewise gives insufficient broadening (≈ 100 meV).[13] However, a sizable contribution to the $1s$ core width comes *indirectly* from the $2s$ electron and the electron-lattice interaction, which is amplified in Li (somewhat like a Sternheimer effect).[14] This may be seen by considering a Wigner-Seitz model of solid Li, and concentrating on boundary-conditions for band-bottom wave functions.

A small change in the local lattice constant, δR, distorts the $2s$ wave function (Fig. 2), causing a small change $\delta\psi(\vec{r})$. The effective charge seen by the $1s$ electron, Z_{1s}, is likewise altered slightly, δZ_{1s}, by the $2s$ electron causing a *relatively* small change $\delta\epsilon_{1s}$ in the $1s$ core energy $\epsilon_{1s}=-Z_{1s}^2\times(13.6\text{ eV})$:

$$\delta\epsilon_{1s}/\epsilon_{1s}\approx-2\delta Z_{1s}/Z_{1s}.$$

But a change in ϵ_{1s} as small as 1% represents a change of order 1 eV.

The effective charge seen by a $1s$ electron has contributions from the nucleus ($Z=3$), the other $1s$ electron, and the $2s$ electron; this last contribution is modulated by the lattice. Thus we write

$$\delta Z_{1s}\approx\delta|\psi(0)|^2\tfrac{4}{3}\pi a_{1s}^3,$$

where we have assumed that the electronic charge density $|\psi(\vec{r})|^2$ is nearly uniform over the $1s$ Bohr radius a_{1s}.

Therefore we estimate the half-width of the $1s$ level due to electron-lattice interaction (in terms of the rms ion displacement δR) to be

$$\tfrac{1}{2}\Delta_{av} \approx |(\delta\epsilon_{1s}/\delta R)\delta R| \approx \frac{-2\epsilon_{1s}}{Z_{1s}} \frac{4\pi a_{1s}^3}{3} \left[\frac{\delta|\psi(0)|^2}{\delta(V/V_0)}\right] \frac{3\delta R}{R_{WS}}. \quad (2)$$

Observe that all the factors in Eq. (2) are well known and can be extracted from experiment. We have $Z_{1s} = 2.69$,[15] $a_B = 0.53$ Å, $a_{1s} = a_B/Z_{1s}$, the Wigner-Seitz radius $R_{WS} = 3.25a_B$, and $\delta R = 0.42$ Å (from neutron-diffraction data).[16] The factor in square brackets can be obtained from the variation of the Knight shift with pressure,[17] and is $\approx 2 \times 10^{-2} a_B^{-3}$; we note that hyperfine data for Li vapor in a He buffer gas, if extrapolated to solid conditions, would give a very much larger number.[18] Hence we find

$$\Delta_{av} \approx 0.46 \text{ eV}, \quad (3)$$

a value somewhat smaller than given by detailed calculations,[19] but certainly large enough to account for the observed 0.5 eV width of the Li threshold[20] in both absorption and emission.[21]

In terms of conventional electron-phonon interaction theory,[22] the phonons dress the $1s$ electron levels, shifting them without any broadening. However, the x ray couples to the *undressed* electron, not to the widthless $1s$ polaron, and its simulated width is $\lambda\hbar\omega_D$, where for Li we estimate $\lambda \approx 13$, $\lambda\hbar\omega_D \approx 0.45$ eV. The crucial point is the large size of λ.

Two prime tests of this model would be (i) a measurement of the edge shape in Li^6 and Li^7, to determine a dependence on isotopic mass,[23] and (ii) high-resolution photoemission measurements.[24] Observe that the model predicts approximately the same temperature dependence for the x-ray edge width and the Knight shift. Both seem to be at most weakly temperature dependent.[17,25,26]

If this electron-phonon mechanism is dominant, the observed angular dependence of γ-ray and electron inelastic scattering cross sections should be significantly less dramatic than the dependence predicted by Doniach, Platzman, and Yue[27] for a Mahan-effect Li edge.

In spirit, this work is similar to Overhauser's direct core-electron–lattice interaction model,[28] as evaluated for Li by McAlister.[29] McAlister's calculation included both band effects and electron-phonon interactions—and found excellent agreement with soft-x-ray data. Bergersen *et al.* subsequently found Overhauser's estimate of the core width to be too large, and concluded that the direct interaction could not account for the Li edge shape. However, the indirect interaction treated here gives a core width comparable to Overhauser's original estimate, and, if used in McAlister's calculation, would restore the substantial agreement with experiment.

In contrast to Overhauser's model, the present indirect-interaction model makes it clear why phonon broadening does not significantly alter the x-ray spectrum of Na: (1) The core hole of Na is $2p$-like, has zero amplitude at the nucleus, and is somewhat less sensitive to changes in $|\psi(0)|^2$; (2) the nuclear charge of Na is 11 not 3, making $\delta Z/Z$ smaller than in Li; (3) the heavier nuclear mass of Na leads to somewhat smaller-amplitude lattice vibrations; and (4) the additional core electrons present in Na but missing from Li can absorb the pressure of the compressed valence electron, further diminishing the effect. We estimate Δ_{av} to be less than 0.1 eV for the L edge in Na. Of course, the K edge in Na should exhibit a significant rounding, but the effect may be obscured by Auger broadening.[30] Thus the large phonon broadening should occur in Li and possibly Be, but its significance in other materials will be governed by the Auger lifetime.

In summary, we have shown that the anomalous rounding of the Li x-ray edge can be explained in a one-electron picture by an electron-amplified indirect interaction between the $1s$ core and the lattice. Final-state interactions, although certainly important, are not necessary to produce the observed anomaly, and may not be dominant in Li. The exact form of final-state effects and the relative importance of phonon effects will have to be determined experimentally.

The Mahan anomalies in Na and Mg will be the subject of a subsequent publication.

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