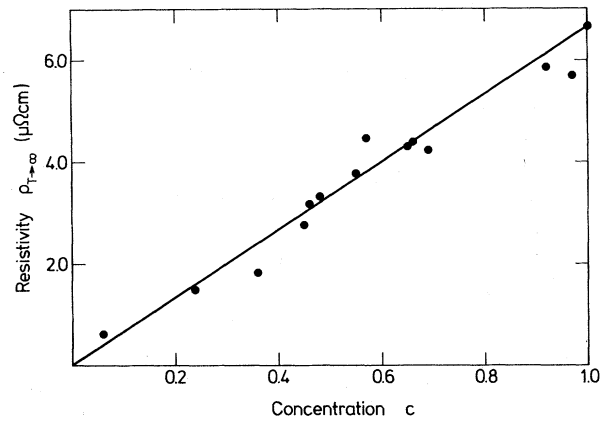

FIG. 2. The concentration dependence of $\rho_{T\to\infty}$ as determined from Fig. 1. The straight line indicates the theoretical prediction.

perature spin-disorder resistivity $\rho_{T\to\infty}$ for each concentration. In Fig. 2 we have plotted this $\rho_{T\to\infty}$ versus c. Indeed we find $\rho_{T\to\infty} \propto c$.

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X-Ray Photoemission from Lithium: An Explanation of Its X-Ray Edge

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Analysis of new Li 1*s* x-ray-photoemission data as a function of temperature unambiguously shows a *large* phonon-broadening contribution and a *small* lifetime width. Our values account *quantitatively* for the observed rounding in all the recent Li *K* absorption-edge measurements.

The rounded *K*-x-ray edge of lithium metal has been the source of controversy for almost thirty years. Following the theory of Mahan, Nozières, and De Dominicis (MND),[1,2] calculations[3-5] of the threshold exponent have all predicted a rounded edge, but one that was insufficiently broad[6] to explain the data.[7,8] This, along with the electron-scattering results by Ritsko, Schnatterly, and Gibbons,[9] has challenged the importance of the MND theory in explaining the Li measurements. Several years before that theory was questioned, McAlister,[10] using a model due to Overhauser,[11] suggested that a transition density of states broadened by phonons could explain the data. Overhauser's model, however, also predicted phonon broadening of the Na edge in excess of the reported width in that material.[12] Bergerson, McMullen, and Carbotte[13] recalculated the phonon broadening for Li and Na and found them both to be considerably smaller than Overhauser's values, but both of comparable magnitude. Dow, Robinson, and Carver,[6] using a different mechanism, made estimates of large phonon broadening for Li and argued for a smaller broadening for Na. Their approach, rebutted by Bergerson, Jena, and McMullen[14] and by Mahan,[5] subsequent-

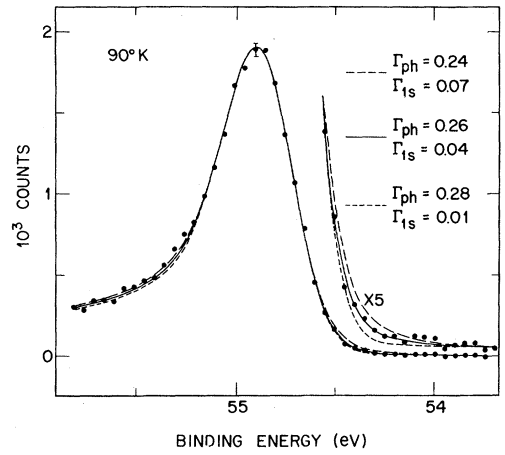

FIG. 1. X-ray-photoemission spectrum showing limits of uncertainty in determining lifetime, Γ_{1s}, and phonon width, Γ_{ph}, in eV (FWHM) for a given singularity index $\alpha = 0.24$ and spectrometer width $\Gamma_{sp} = 0.25$ eV.

ly received experimental support from the temperature dependence of the Li absorption edge reported by Kunz, Peterson, and Lynch.[15] However, Peterson's[16] recent work suggests that the existence of a strongly phonon-broadened edge is not so important and argues instead that a transition density of states is the dominant rounding mechanism. Finally, a short Li 1*s* lifetime has been suggested by Franceschetti and Dow[17] and by Mahan[5] as yet another possible source of broadening. In this Letter we report new x-ray-photoemission-spectroscopy (XPS) data which unambiguously establish the magnitudes of the individual broadening mechanisms. Our values are shown for the first time to explain quantitatively the observed rounding in all[9,15,16] the Li-edge measurements.

The XPS data were obtained with an AEI 100 spectrometer modified for operation with monochromatized Al $K\alpha$ x rays.[18] The response function of the instrument is approximately Gaussian with a full width at half-maximum (FWHM) of 0.25 ± 0.02 eV. High-purity (99.99%) samples were repeatedly evaporated *in situ* at base pressures of 10^{-11} Torr onto smooth substrates at room temperature. Measurements at room temperature were made before and after each low- (90°K) and high-temperature (440°K) run. Each data set at low and high temperatures represents a sum of three runs; that at room temperature represents the summation of all the room temperature runs.

The asymmetry of the Li 1*s* peak is apparent in Fig. 1. The tails of the bulk and surface plasmons appearing 7.45 and 3.95 eV[19] from the main peak do not influence its shape significantly. The asymmetry is a manifestation of the response of the many-electron system to the sudden creation of a core hole.[20] Using the line-shape function due to Doniach and Šunjić (DS)[21] we attempted to analyze the Li data following procedures previously described.[22] Briefly, the DS function of singularity index α and hole-state lifetime width Γ is convoluted with the spectrometer response function of known FWHM Γ_{sp}. Attempts to fit the Li data using this procedure proved very unsatisfactory, but convolution with an *additional* Gaussian function gave an excellent fit. Based on the temperature dependence (see below) and functional form of this additional contribution we attribute it to phonon broadening and denote its FWHM by Γ_{ph}.

We demonstrate in Fig. 1 the procedure by which Γ_{ph} is determined and the limits of its uncertainty using the Li 1*s* data at 90°K. It is seen that the low- and high-binding energy sides of the peak jointly constrain the choices of Γ_{ph} and the 1*s* hole-state lifetime Γ_{1s} to limits of ± 0.02 eV; the uncertainty in the spectrometer function increases this to ± 0.04 eV. The choice of α is less sensitive to Γ_{ph} and Γ_{1s} and has uncertainty limits of ± 0.010, arising largely from the uncertainties in Γ_{ph} and Γ_{1s} and data statistics. We have chosen to fit the data over an interval ~ 1.5 eV from the peak in which the DS function should be a good approximation and in which the interference from inelastically scattered electrons is negligible.[23]

The Li 1*s* data at three temperatures are shown in Fig. 2 together with the fitted line shapes and corresponding parameters. Their values have important implications. The Li 1*s* lifetime is considerably smaller than the previously proposed values of 0.13 eV[17] and 0.2–0.3 eV.[5] *Our result therefore rules out lifetime broadening as an important mechanism for the rounding of the Li K edge.* The values of α, which range between 0.24 and 0.25, are larger than that of 0.18 ± 0.03 reported by Ley *et al.*[24] Note that an essentially constant choice of Γ_{1s} and α fit the data consistently well at all temperatures, as theory requires. The Friedel sum rule and our measured α yield a threshold exponent[1,2] $\alpha_1 = -0.13$,[25] in good agreement with previous calculations[3-5] but insufficiently negative[6] to explain the Li-*K*-edge data.

The parameter Γ_{ph} determined in Fig. 2 is of *appreciable* magnitude and increases monotoni-

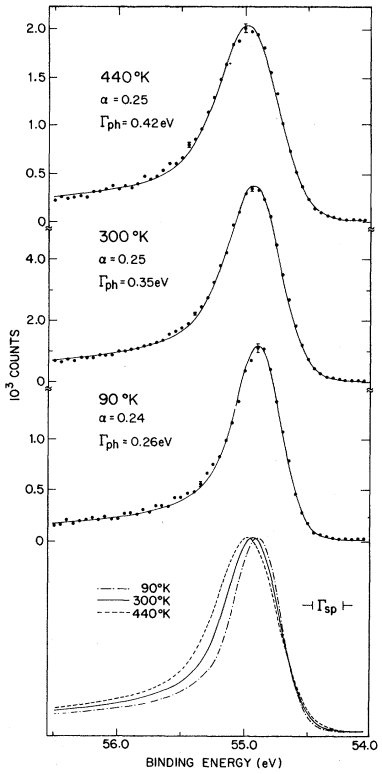

FIG. 2. Li 1*s* XPS spectra at 90, 300, and 440°K. $\Gamma_{1s} = 0.04$ eV and $\Gamma_{sp} = 0.25$ eV for all fits. Note large increase in Γ_{ph} with increasing temperature.

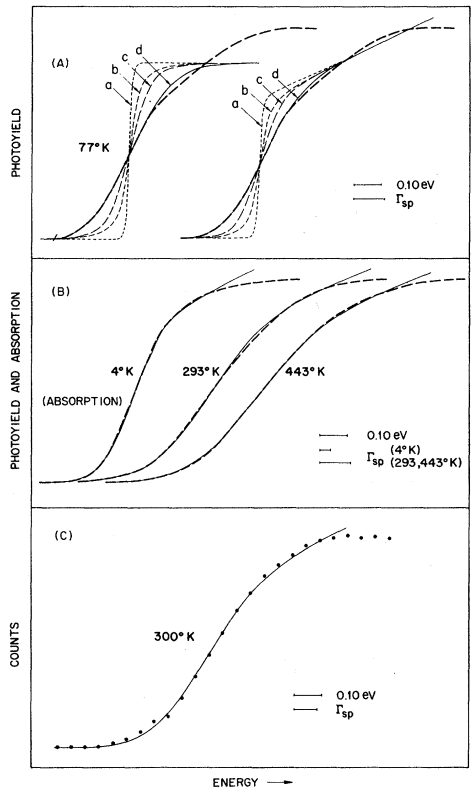

FIG. 3. Li *K* edge data from (a) Ref. 16, (b) Ref. 15, and (c) Ref. 9. The dark dashed lines in (a) and (b) and the points in (c) are the experimental data. See text for details.

cally with increasing temperature. If we compare[23,26] the experimentally determined XPS Gaussian broadening in Li (see Fig. 2) with the predictions of various theories[6,11,13,27] it is clear[26] that *none* of the theories accurately describes the *magnitude* of the broadening, but *all* yield a *temperature dependence*, $\Gamma_{ph}^{-1} d\Gamma_{ph}/dT$, in good agreement with our measurements.

This result represents the first direct observation of phonon broadening in photoemission from a metal.[28] More importantly, it demonstrates unambiguously that *hole-phonon coupling is an extremely important phenomenon in Li.*

What do the above results imply about the interpretation of Li-edge measurements? The fact that our XPS measurements are completely unaffected by transition density of states (TDOS) and the fact that we have firmly established a Li 1*s* lifetime value of 0.04± 0.03 eV now allows for the analysis of the data from Refs. 9, 15, and 16 with only the phonon-broadening value as an adjustable parameter. In Fig. 3(a) we illustrate our analysis procedures using the most recent data from Ref. 16 and assuming either a constant TDOS, left-hand case, or a TDOS after McAlister[10] as suggested in Ref. 16, right-hand case. Curve *a* is a Fermi function at $T = 77$°K, curve *b* is curve *a* convoluted with a (assumed) Gaussian spectrometer function of 0.11 eV (FWHM),[16] and curve *c* is curve *b* convoluted with a Lorentzian lifetime value of 0.04 eV. Comparison of curves *c* with the data shows that independent of TDOS model additional broadening is required. Convoluting curves *c* with additional Gaussian components, $\Gamma_{ph} = 0.21$ eV or 0.23 eV (left- and right-hand cases, respectively) gives an excellent fit to the data, curves *d*, and shows that the TDOS of Ref. 10 is the better choice for the upper part of the Li *K* edge.[29] We have analyzed the data of Refs. 15 and 9 using the above procedures and the TDOS from Ref. 10. The results are shown in Figs. 3(b) and 3(c). The values of Γ_{ph} in eV (FWHM) for the different data sets at various temperatures are 0.18 (4°K),[15] 0.21 (77°K),[16] 0.33 and 0.35 (300°K),[15,9] and 0.38 (443°K).[15] The precision of the above fits is ± 0.02 eV, while the accuracy, which depends on the unspecified uncertainty of Γ_{sp}, is undoubtedly somewhat larger.

Comparison of these values with those determined from the present XPS work clearly demonstrate that appreciable phonon broadening very similar (i.e., within experimental error) to that observed in XPS is present in all the Li-K-edge data. This result, along with the fact that its magnitude is relatively insensitive to the choice of TDOS used, shows that *hole-phonon coupling is the dominant rounding mechanism of the Li K edge.*

In summary, we have shown that phonon broadening is an important mechanism in both x-ray photoemission and edge data from Li, but that no available theory consistently describes its magnitude. We have also ruled out lifetime broadening and a large negative threshold exponent as important contributions to the rounding of the Li K edge. We therefore conclude that a transition density of states broadened by very strong hole-phonon coupling is responsible for the observed shape of the edge in Li.

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