Auger Broadening Correction to the Low-energy tail of the Lithium X-ray K-emission spectrum

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Abstract

In this work the actual contribution of the Auger effect to the broadening of the low-energy end of the K-emission spectrum of metallic lithium is investigated and calculated. By applying the relevant selection rules and transition probability for the Auger process to the Auger rate, an Auger width of $0 \cdot 01eV$ *is obtained. When this result is incorporated into existing calculations for the lithium spectrum, there is an appreciable elimination of the low-energy blur existing between the final spectrum and the experimental spectrum of* Tomboulian and Bedo (1958)

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1.0 Introduction

Interest in the soft x-ray emission for solids stems from the threshold singularity at the Fermi edge for metals and from the observed broadening of the emission band on the low energy side. Added to this is the fact that x-ray emission is capable of giving information on the individual energy levels of the conduction or higher bands. The soft x-ray emission spectrum does not reproduce the valence-electron density of states curve. This is because the contribution from many-body effects and is especially so for the K-emission bands. However, for those elements hat have both K and L bands, the L-emission spectra tend to follow the density of states curves apart from the threshold region. Theoretically, the low energy intensity should follow the $E^{\frac{3}{2}}$-law. But most evident is the broadening of the spectrum in that energy region. Several factors have been attributed to the low energy blur. These include the effect of the valence hole lifetime, as well as multiple transitions, e. g. shake-up and radiactive Auger processes, and of course phonon transition effects. In addition, there is the belief that plasmon satellite also contributes to the low-energy tail. A plasmon satellite occurs when the emission is accompanied by a plasma excitation and therefore the emitted photon energy is diminished by the corresponding plasma frequency. That means that, on the lower-energy side of the emission, one expects to find a feature that resembles the main emission band, but in which the (independent) collective mode of the quasi-particle (Plasmon) dispersion broaden much of the structure. In soft x-ray emission, the plasmon satellites are in fact observed to be 1 to 3% of the main valence-band emission, and lie on a background produced by the multi-electron transitions. The plasmon satellites leading to valence-band broadening are a direct consequence of the electron-electron excitations that accompany the radiative transition of an electron from the valence band to the empty core level. It is to be noted however, that there are conflicting reports about the dominant process responsible for the broadening in several substances. In the case of sodium $L_{II\text{-}III}$ band for example, Landsberg (1949) concluded that the lifetime broadening is the dominant process, while Pirenne and Longe (1964) conclude that the low energy tail is due mainly to multiple transition. Invariably the different processes contribute to the broadening. For example, Livins et al (1988) observed from their calculation for diamond that there is a sensible shake-up tail upon which a plasmon satellite rests.

For Lithium, interest in the soft x-ray spectrum appears to have been concentrated in the threshold region where there is a premature peak about $0 \cdot 6eV$ below the high-energy threshold. By incorporating many-body effects near the threshold as introduced by Nozieres and de Dominics (ND) (1969) or Maham (1974) it has been possible to obtain concurrence between the computed spectrum and the experimental spectrum in that region. Some investigations have also been reported on the low energy broadening.

These include McAlister (1969) who investigated phonon broadening, obtaining specific full width at half-maximum (FWHM) for the metal. Also Ferrell (1969) gave an estimate of the thermal broadening of the spectrum. In the case of Auger broadening, Crasemann (1991) gave selection rules and transition probability for the Auger effect, while Franceschetti and Dow (1974) made some direct calculations of the Auger edge width. Also Bahl et al (1979) obtained the relation for calculating the kinetic energy of the Auger electrons.

In this investigation, the actual contribution of Auger effect to the broadening of the low energy end of the K-emission spectrum of metallic lithium is fully investigated and computed. Wentzel's quantum mechanical theory of radiationless transition (see Warren et al, 1967) is invoked in the transition matrix from which applicable selection rules for finding the Auger width is derived. In the calculation the contribution of Bahl et al (1979) is applied in finding the valence band maximum (VBM) and the full width at half-maximum (FWHM) for the auger transition. The result is applied to the computed x-ray emission spectrum of Mgbenu et al (1978) and the final spectrum is compared with experimental results.

2.0 Auger Calculations for Lithium

The kinetic energy T of an electron making an Auger (a radiationless) transition from state LL with energy $\in_{LL}$ to state K with energy $\in_K$ is of the form

$$T = \frac{mv^2}{2} = \in_K - \in_{LL} \tag{2.1}$$

A linear combination of such Auger transitions (energies) possibly enhances the blur at the low energy tail of the lithium x-ray K-emission curve. The Auger rate is given by Wentzel (1927) (see Warren et al, 1967) as

$$W_A = \frac{2\pi}{\hbar}\int_f |D|^2 \delta(\in_f \in_i) ds_f \tag{2.2}$$

where D is the transition matrix, which, for such a direct transition, is of the form

$$D = \iint \psi^*_{n''\ell''j''}(i)\psi_{\alpha\ell_A j_A}(f)\frac{|e^2|\psi_{n\ell j}}{|r_{if}|}(i)\psi_{n'\ell'j'}(f)d\tau_i d\tau_f \tag{2.3}$$

The nlj's characterize the electrons in specific quantum states with $\alpha\ell_A j_A$ depicting the electrons in the continuum (Auger state.)

The Auger rate is moderated by the relevant selection rules for an Auger transition, and of course the probability that an electron in a higher state will actually undergo the transition. The former moderator requires that the total angular momentum and the parity of the final state system (ion plus emitted electron) be the same as those of the initial state ion, while the latter depends on the weighting (peripheral) factors coupling the states. A calculation allowing for these gave a relative probability of approximately 10^{-3} for Auger transition in lithium during a typical K-emission process of the metal. The Auger rate is further enhanced by a contribution to the Auger-electron energy, typically of the order of 10eV, from extra-atomic relaxation.

In this calculation of the Auger-electron energy the approach of Bahl et al (1979) is employed, taking into cognizance the band-bending shift, the extra-atomic relaxation and the binding energy with its accompanying Coulomb matrix elements (in the quantal derivation.) The analysis gives a kinetic energy shift

$$\Delta T = -\Delta \in +3\Delta R \tag{2.4}$$

where $\Delta \in$ is the shift due to the initial state charge while ΔR is the contribution arising from the extra-atomic relaxation. The binding energy shift $\Delta \in_B$ relative to the valence band maximum VBM (at the fermi level) is given by

$$\Delta \in_B = \Delta \in -\Delta R \tag{2.5}$$

Summing equations (2.4) and (2.5) gives

$$\Delta T + \Delta \in_B = 2\Delta R \tag{2.6}$$

A further (similar) analysis outside the fermi level and extending towards the continuum gives

$$\Delta T + \Delta \in_B = 3\Delta R \tag{2.7}$$

Two lithium K-edges are obtainable from the extrema (2.6) and (2.7): a lower limit of 0.13eV and an upper limit of 0.003eV respectively. Based on the estimates of Crasemann the value of ΔR is the order of 10eV. Thus the

core-level shift of the Li K-emission spectrum is given by $20-0\cdot13$ to $30-0\cdot13$ (i.e. $19\cdot87$ to $29\cdot87$)eV for the lower limit, and $20-0\cdot003$ to $30-0\cdot003$ (i.e. $19\cdot997$ to $29\cdot997$)eV for the upper limit. This implies that the least shift in the core-level energy due to the Auger effect is 19.87eV, while the maximum shift due to the same effect is 29.997eV, for the Li K edge.

The above extrema are moderated by the Auger transition probability for metallic lithium. The value furnished by Crasemann [3] for this quantity is 0.001. Incorporating this quantity into the above values gives Auer broadening extrema of 19.87 x 0.001 = 0.001987eV and 29.997 x 0.001 = 0.029997eV respectively. Consequently, an "on-hand" Auger width for lithium based on this probability figures is 0.029997 – 0.01987 = 0.01eV approximately.

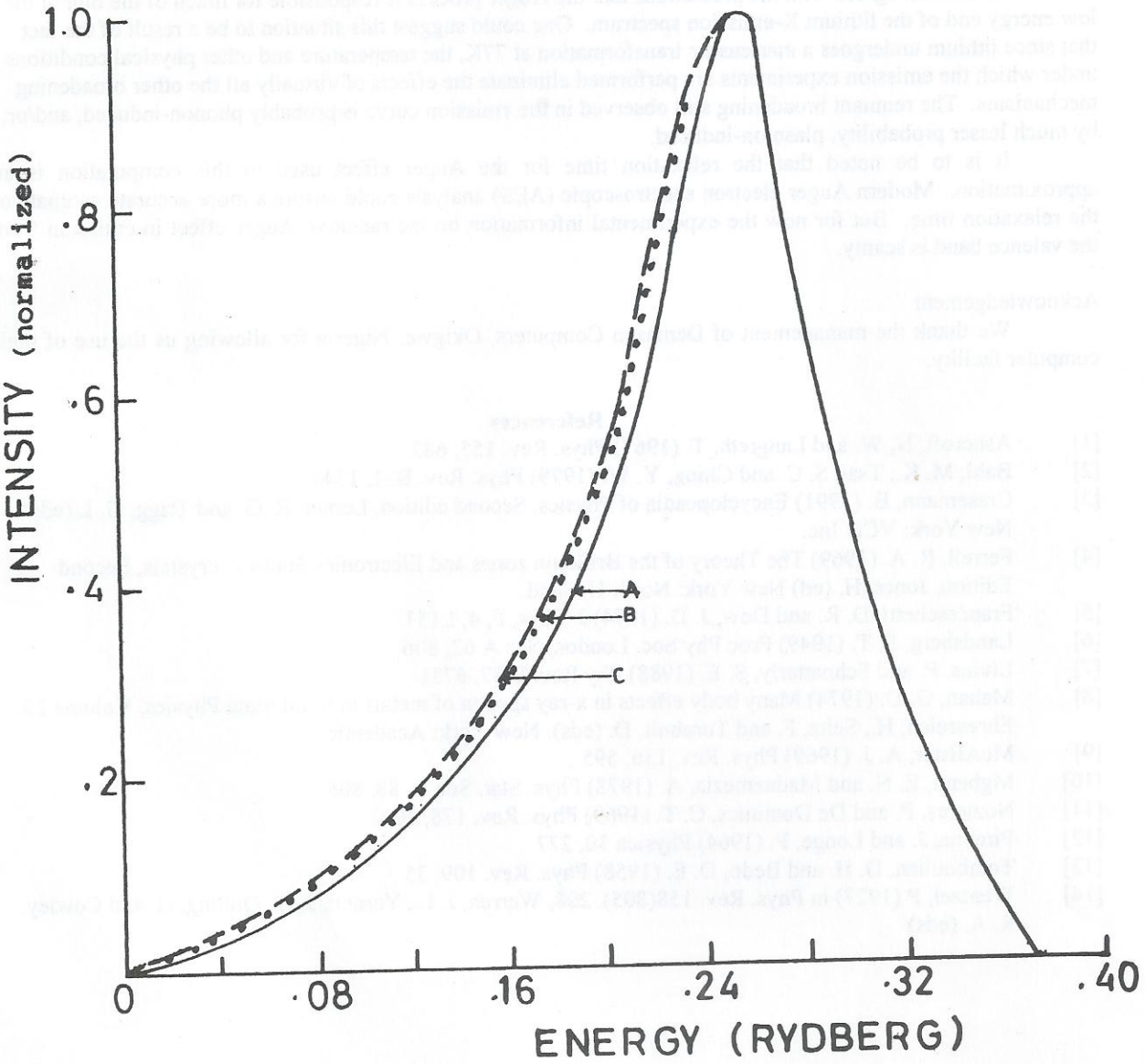

Figure1: Emission profiles for metallic lithium
A – computed spectrum without broadening correction (Mgbenu and Maduemezia [10])
B – computed spectrum with Auger broadening correction (by this work)
C – experimental spectrum (Tomboulian and Bedo [13])

3.0 Result and Discussion

Several calculations of the lithium K-emission and absorption spectra are readily available. Most of the computed spectra, for example, Mgbenu et al (1978) and Ashcroft et al (1967) agree for the most parts with the experimental work of Tomboulian and Bedo (1958). The former computation applied the many-body theory of Nozieres and de Dominics (1969) in the neighbourhood of the Fermi edge to their AKPW calculation, while the latter used the pseudo-potential approach with the many-body theory. When the ensuring Auger with width of 0.01eV is applied to the computed spectrum by Mgbenu et al, the Auger correction significantly narrows down the broadening observed in the low energy tail of the lithium x-ray K-emission spectrum as shown in Figure 1

This result agrees with the predictions that the Auger process is responsible for much of the blur at the low energy end of the lithium K-emission spectrum. One could suggest this situation to be a result of the fact that since lithium undergoes a martensitic transformation at 77K, the temperature and other physical conditions under which the emission experiments are performed eliminate the effects of virtually all the other broadening mechanisms. The remnant broadening still observed in the emission curve is probably phonon-induced, and/or, by much lesser probability, plasmon-induced.

It is to be noted that the relaxation time for the Auger effect used in this computation is an approximation. Modern Auger electron spectroscopic (AES) analysis could ensure a more accurate estimate of the relaxation time. But for now the experimental information on the radiative Auger effect in emission from the valence band is scanty.

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