1096
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Electron probe microanalysis of transition metals using L-lines: the effect of self-absorption

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The use of soft X-rays (1 < keV) for electron probe microanalysis (EPMA) poses numerous difficulties mainly because soft X-rays involve valence electrons, which are affected by chemical bonding, and matrix corrections do not account for bonding effects [1]. Because of that, alternative strategies are being developed [2]. In the case of the main L-lines of the first-row transition metals, the situation is further complicated by the effect of self-absorption. This is so because these lines are located close to the L_2 and L_3 absorption edges and the high-energy side of the lines straddle the rising L-edges. As a result, there is a distortion of the shape and position of the lines with incident electron energy. Although the effect of self-absorption has been known for decades (mainly from soft X-ray spectroscopic studies of solids [3]), there is still little understanding of its implications in quantitative EPMA analysis. In this study, we assess the influence of self-absorption on the Lα lines emitted from metallic Fe, Ni, Cu and Zn targets. X-ray emission lines are modelled as Lorentzian distributions, with intensities obtained from Monte Carlo simulations [4], and self-absorption is evaluated numerically by using experimental energy-dependent mass absorption coefficients, $(\mu/\rho)(E)$, where E is the photon energy, and X-ray depth-distributions obtained from Monte Carlo simulations. For comparison purposes, self-absorption is also evaluated using a definite mass absorption coefficient, (μ/ρ), which is the conventional approach used in matrix corrections.

Figure 1a shows the theoretical Ni Lα emission line (a Lorentzian profile with a natural width of 2.58 eV [5]), and the energy-dependent mass absorption coefficients of metallic Ni measured by Ménesguen et al. [6]. Both the emission line and the absorption edge are relatively broad and overlap is considerable; as a result, $(\mu/\rho)(E)$ increases rapidly across the X-ray emission line. Figure 1b compares the emitted Ni Lα line for 30 keV electron excitation evaluated using the mass absorption coefficients of Ménesguen et al., with that obtained using a fixed mass absorption coefficient of (μ/ρ)=3772 cm^2/g, i.e., the value measured by the same authors at the central energy of the Ni Lα line (E=851.47 eV). There is a considerable distortion of the line shape when self-absorption is calculated using $(\mu/\rho)(E)$, which results in a shifting of the line position towards lower energy and a ~15% increase of its peak height. This suggests that, in this case, even if we know accurately the mass absorption coefficient at the line energy (e.g., from first-principle calculations [7] or experimental measurements [6]), errors of up ~15% can still be made if self-absorption is not accounted for. The observed intensity difference decreases with decreasing incident electron energy and becomes negligible below ~5 keV (Fig. 1c). This trend is confirmed when both the diagram and satellite lines are included in the calculations and the resulting spectrum is convolved with a Gaussian distribution to account for spectrometer broadening. Because the structure and position of the rising $L_{2,3}$-edge depends on the chemical bonding, for Ni compounds the degree of self-absorption will vary depending on the compound, leading to errors in the evaluated concentrations.

Calculations for metallic Fe show similar results than those for metallic Ni. In contrast, self-absorbed X-ray intensities evaluated for metallic Zn and Cu using $(\mu/\rho)(E)$ do not differ significantly from those obtained using a single (μ/ρ) value. This is so because for metallic Zn and Cu, there is almost no overlap between the emission Lα,β-line and the absorption $L_{2,3}$-edge. However, overlap may exist for some Cu and Zn compounds [8].

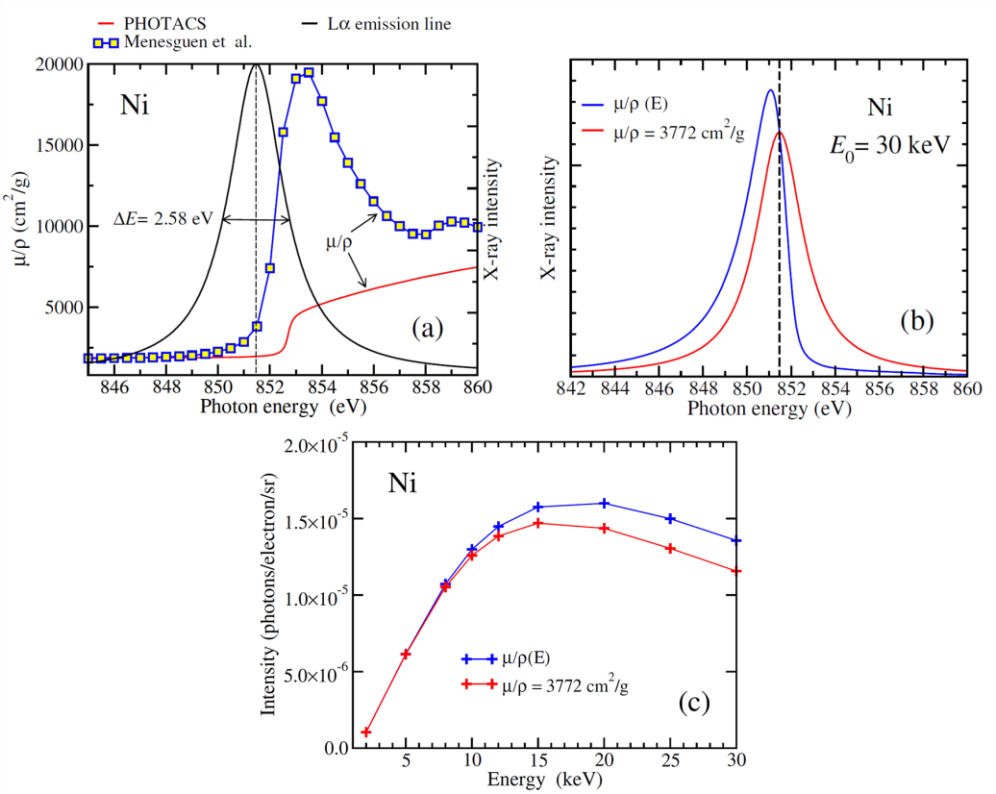

Figure 1. Ni Lα emission line and theoretical (PHOTACS [7]) and experimental (Ménesguen et al. [6]) mass absorption coefficients of Ni (a). Comparison of self-absorbed Ni Lα emission lines for 30 keV electron excitation (b) and X-ray intensities as a function of incident electron energy (c) calculated with the energy-dependent mass absorption coefficients of Ménesguen et al. (μ/ρ(*E*)) and with (μ/ρ)=3772 g/cm^2.

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