

Valence Electron Energy-Loss Spectroscopy as a Tool for *In Situ* Diagnostics of Materials Properties

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Valence EELS between 0-50 eV energy losses allows direct, high spatial resolution determination of a number of electronic, dielectric and optical parameters of solids (intra/inter band transitions, excitons; surface, defect and interface states, band gap, dielectric permittivity, optical constants, and joint density of states). One of the major inelastic scattering events in this range is the generation of quantized high-frequency ($\sim 10^{16}$ Hz) correlated longitudinal electron excitations (plasmons) by fast electrons passing through a thin specimen. Plasmons are potentially useful for probing various states of matter because the volume plasmon energy, E_p , is related to the valence electron density, n , by a resonance angular frequency, ω_p : $E_p = \hbar\omega_p \cong [(\hbar\omega_p^f)^2 + E_g^2]^{0.5}$ [1], where $\omega_p^f = [ne^2/(\epsilon_0 m)]^{0.5}$ is the free electron plasma frequency, e is the electron charge, ϵ_0 is the permittivity of vacuum, and m is the electron mass, E_g is the bandgap energy (for semiconductors and some insulators, $E_g^2 \ll E_p^2$, so $E_p \cong \hbar\omega_p^f$). The relation between E_p and n allows determination of solid-state properties that are governed by the ground-state electron density. As was shown recently, it is possible to evaluate the mechanical and transport properties of materials from correlation charts of the related parameters vs. E_p [2-4]. Moreover, we found that these relations demonstrate universality and scaling and follow the universal binding energy relation (UBER, [5]), which originates in the nature of electron-ion (atom nuclei) interactions and in the essentially exponential decay of electron density with interparticle separation or into interstitial regions described by a universal function of the Rydberg type [6]. Variations in the electron density at the boundary of the Wigner-Seitz (WS) cells, n_b , cohesive energy per atomic volume, E_{coh}/V_{wse} , the bulk modulus, B_m , and E_p with atomic number (Fig. 1a,b) exhibit generally similar periodicities and parabolic behavior within each transition series, starting from the 2nd period, although with different scales of variation. As a consequence, one can obtain strongly correlated log-log scaling of the power law type, $P_m = AE_p^B$, where P is the property and A and B are least squares fitted parameters. Fig. 2 presents such relationships for (a) E_{coh}/V_{wse} and (b) B_m , for cubic single-crystals. Using a free-electron (FE) approximation for a cubic lattice with the number of valence electrons, N_{ve} , one can directly relate B_m to E_p taking into account three basic terms (electrostatic attraction and repulsion and kinetic energy) with no correlation and exchange corrections [3]:

$$B_m = 7.29N_{ve}(me/h^2)^2E_p^2 = 0.194N_{ve}E_p^2 \text{ (GPa)}. \quad (1)$$

For isotropic matter, this leads to connections among the bulk, elastic and shear moduli and E_p :

$$Y_m = 3(1-2\nu)B_m = 9e^2(1-2\nu)/40\pi r_0^4 = 21.9(1-2\nu)(me/h^2)^2N_{ve}E_p^2 = 0.582(1-2\nu)N_{ve}E_p^2 \text{ (GPa)} \quad (2)$$

$$G_m = 10.9[(1-2\nu)/(1+\nu)](me/h^2)^2N_{ve}E_p^2 = 0.291[(1-2\nu)/(1+\nu)]N_{ve}E_p^2 \text{ (GPa)}. \quad (3)$$

The curves for Y_m and G_m calculated using Eqns. (2, 3) and average values of Poisson's ratio [3] are shown in Fig 3. The FE-approximation with no matching parameters satisfactorily describes the behavior of simple metals and qualitatively follows the trends in elastic constants for polyvalent elements. In a field-emission analytical electron microscope, where sub-nanometer electron probes can be obtained that provide atomic-level spatial resolutions of 0.08-0.2 nm with 0.7-1.7-eV energy resolution, such correlations enable *in situ* evaluation of the intrinsic local solid-state properties of materials without any special set-up and when it is difficult or impossible by other means. This was

previously illustrated by analyses of nanoprecipitates of the θ' -Al₂Cu and γ -TiH_x phases in alloys [3, 8].

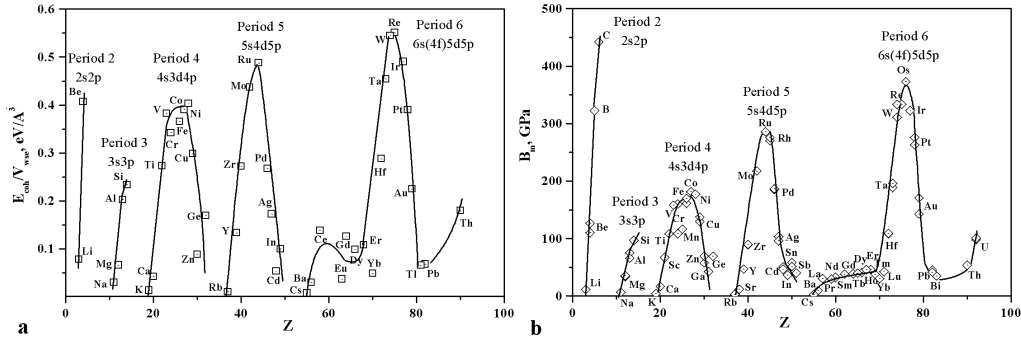


FIG. 1. (a) $\Delta E_{coh}/V_{wse}$ and (b) B_m of elements vs. atomic number Z .

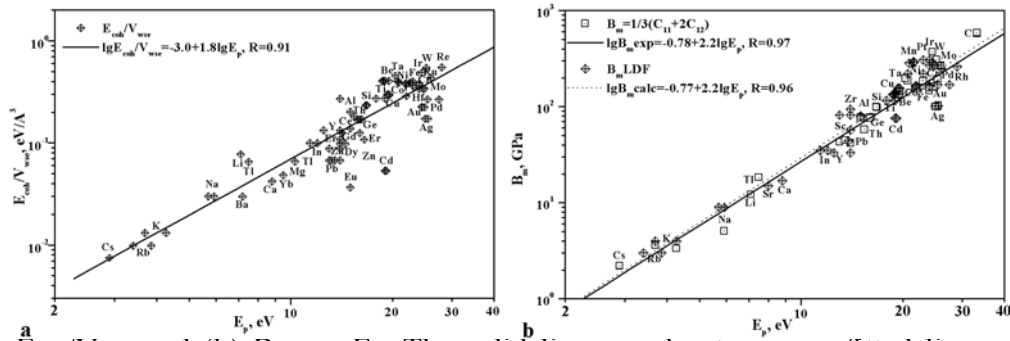


FIG. 2. (a) E_{coh}/V_{wse} and (b) B_m vs. E_p . The solid lines are least squares fitted linear regressions (LSF-LR) for 24 cubic single-crystal metals, C, Si and Ge, determined experimentally and calculated by the KKR-LDF method [7].

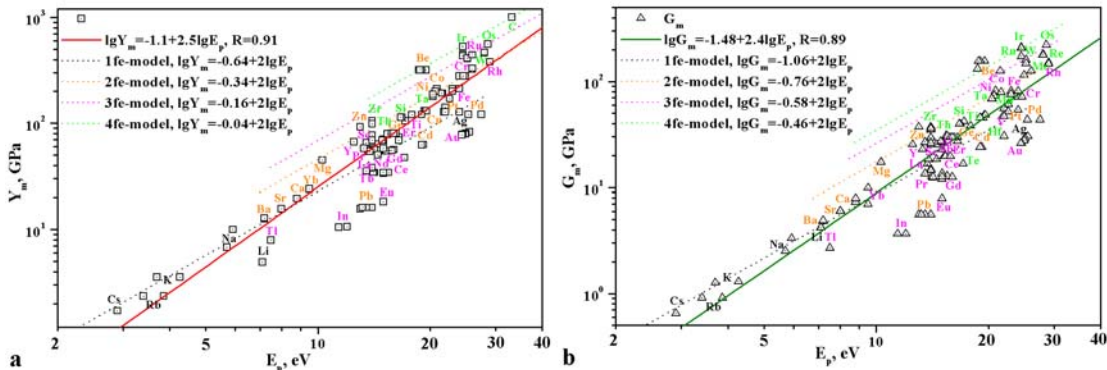


FIG. 3. Elastic constants for 58 polycrystalline metals, B, C, Si, Ge, Tl and Te vs. E_p : (a) Young's modulus, Y_m and (b) shear modulus, G_m . The solid lines are LSF-LRs. Dash lines denote estimations by the FE-model. Typical element valencies are shown by different colors: 1 (black), 2 (orange), 3 (magenta), 4 and higher (green).

References

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