Effect of Core Polarization on the Plasma Frequency of Cd, In, and Sn

E. Zaremba[(a)] and K. Sturm
Institut für Festkörperforschung, Kernforschungsanlage Jülich, D-5170 Jülich, West Germany
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The plasma frequencies of Cd, In, and Sn are determined from a calculation of the long-wavelength, frequency-dependent dielectric function. The mutual interaction between core- and valence-electron charge fluctuations is included within the random-phase approximation. Core polarization is shown to be an important effect and its inclusion leads to values of the plasma frequency in excellent agreement with experiment.

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It has long been realized that core polarization can influence the dielectric properties of metals.[1] However, relatively little has been done in the way of quantitatively estimating its effect on, for example, the plasma frequency. The metals Cd, In, and Sn are of particular interest in this regard since they have well-defined plasma excitations whose frequencies, however, differ markedly from the free-electron estimate $\omega_p^0 = (4\pi n_0 e^2/m)^{1/2}$ as given by the mean valence-electron density n_0 (see Table I). That this deviation is due in part to the polarization of the ionic cores, with its consequent effect on the dynamics of the valence electrons, is consistent with the observed trend on going from Cd to Sn. The decreasing frequency shift correlates with the decrease in core polarizability that would be expected as the $4d$ core band progressively narrows and moves down in energy relative to the free-electron conduction band. The theory presented in this paper confirms this physical explanation, and detailed calculations lead to results in quantitative agreement with experiment.

Because of the inhomogeneous nature of solids, core as well as valence electrons experience local electric fields which differ from the average macroscopic field. Whereas these so-called local field effects (LFE) are often neglected in calculations of the optical properties of metals, they become essential when treating the dipolar coupling between charge fluctuations localized on different sites. In the case of insulators, LFE can be accounted for by means of the Clausius-Mosotti (CM) expression for the dielectric constant. In metals, the core and valence charge fluctuations are coupled and the inclusion of LFE is correspondingly more difficult. Nevertheless, as we shall see, the effects of core polarization can be included by using an expression of the CM form with a suitably defined frequency-dependent core polarizability.

TABLE I. Plasma frequencies (electronvolts): free-electron (ω_p^0), valence (ω_p^*), and theoretical and experimental.

Metal (r_s)	ω_p^0	ω_p^*	ω_p Theory	ω_p Expt.
Cd (2.59)	11.3	13.2	8.5	7.0–9.5[a]
In (2.41)	12.6	14.0	11.5	11.4[b]
Sn (2.22)	14.2	15.5	13.9	13.7[c]

[a]Aiyama and Yada (Ref. 2), and Feuerbacher and Fitton (Ref. 3).
[b]Reference 2, and Raether (Ref. 4).
[c]Reference 4.

Quite generally, the long-wavelength ($\mathbf{q} \to 0$) macroscopic dielectric function of a periodic solid is determined by

$$\epsilon(\omega) = \phi^{\text{ext}}(\omega)/\phi^{\text{tot}}_{\mathbf{G}=0}(\omega), \tag{1}$$

where $\phi^{\text{ext}}(\omega)e^{i\mathbf{q}\cdot\mathbf{r}}$ is the externally applied potential and $\phi^{\text{tot}}_{\mathbf{G}}(\omega)$ is the Fourier amplitude of the total microscopic potential at the reciprocal lattice vector $\mathbf{G}$. Most calculations of the dynamic dielectric response are at the level of the random-phase approximation and we adopt the same approximation here. Accordingly, the charge density induced by ϕ^{ext} is determined from the equations

$$\delta n(\mathbf{r},\omega) = \int d^3r'\, \chi^0(\mathbf{r},\mathbf{r}',\omega)\phi^{\text{tot}}(\mathbf{r}',\omega), \tag{2}$$

with

$$\phi^{\text{tot}}(\mathbf{r},\omega) = \phi^{\text{ext}}(\mathbf{r},\omega) + \int d^3r'\, \delta n(\mathbf{r}',\omega)/|\mathbf{r}-\mathbf{r}'|. \tag{3}$$

The density response function appearing in (2) can be expressed in the convenient form

$$\chi^0(\mathbf{r},\mathbf{r}',\omega) = \sum_{\mathbf{k}n} \psi^*_{\mathbf{k}n}(\mathbf{r})\psi_{\mathbf{k}n}(\mathbf{r}')f(\mathbf{r},\mathbf{r}',\epsilon_{\mathbf{k}n},\omega), \tag{4}$$

where the summation extends over all occupied Bloch states $\psi_{\mathbf{k}n}(\mathbf{r})$ with band energy $\epsilon_{\mathbf{k}n}$. The factor f can be written either as a sum over unoccupied states or in terms of the crystal Green's function.[5,6] The important point for the subsequent development is that it depends on the indices $(\mathbf{k}n)$ only through the eigenvalue $\epsilon_{\mathbf{k}n}$.

Individual core- and valence-electron charge fluctua-

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tions can be isolated by writing

$$\chi^0(\mathbf{r},\mathbf{r}',\omega)=\chi_c^0(\mathbf{r},\mathbf{r}',\omega)+\chi_v^0(\mathbf{r},\mathbf{r}',\omega), \tag{5}$$

where the two terms involve a summation in (4) over core (c) and valence (v) states, respectively. For narrow core bands, $\epsilon_{\mathbf{k}n}\approx\epsilon_n$, and f is approximately independent of $\mathbf{k}$. The $\mathbf{k}$ sum in (4) can then be performed explicitly and one finds that

$$\chi_c^0(\mathbf{r},\mathbf{r}',\omega)=\sum_l \chi_a^0(\mathbf{r}-\mathbf{R}_l,\mathbf{r}'-\mathbf{R}_l,\omega), \tag{6}$$

where χ_a^0 is an atomic-like response function localized at each site $\mathbf{R}_l$.

With the site response functions defined, the solution of (2) and (3) is effected by the separation $\delta n=\delta n_c+\delta n_v$, where the core density $\delta n_c=\sum_l \delta n_c^l$ is a sum of site densities. The core charge density δn_c^l on the lth site is driven by the total potential which has contributions from (i) the external field, (ii) the induced potential due to all other core charges $\delta n_c^{l'}$ ($l'\neq l$), (iii) the induced potential due the valence charge, and (iv) the potential due to δn_c^l itself. Because of the localized nature of the core, we can expand contributions (i)–(iii) about the position of the central site ($l=0$). To lowest order, the core change on this site is determined by the equation

$$\delta n_c^0(\mathbf{r},\omega)=\int d^3r'\,\chi_a^0(\mathbf{r},\mathbf{r}',\omega)\times[-\mathbf{r}'\cdot\mathbf{E}_0+\phi_0(\mathbf{r}',\omega)], \tag{7}$$

where $\mathbf{E}_0$ is the local electric field due to all charges exclusive of δn_c^0, while ϕ_0 is the electric potential of δn_c^0 itself. Equation (7) constitutes an integral equation for δn_c^0 which is identical in form to that used so successfully in calculations of atomic photoabsorption cross sections.[6] Its solution can be used to define a core polarization $\delta n_c^0(\mathbf{r},\omega)=\mathbf{p}_0(\mathbf{r},\omega)\cdot\mathbf{E}_0$ and a core polarizability according to

$$\alpha(\omega)=\tfrac{1}{3}\int d^3r\,\mathbf{r}\cdot\mathbf{p}_0(\mathbf{r},\omega). \tag{8}$$

In terms of these quantities the total microscopic potential satisfies the equation ($\phi^{\text{ext}}=1$)

$$\phi_{\mathbf{G}}^{\text{tot}}(\mathbf{q},\omega)=\delta_{\mathbf{G},0}+\frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2}\sum_{\mathbf{G}'}\chi_v^0(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}',\omega)\phi_{\mathbf{G}'}^{\text{tot}}(\mathbf{q},\omega)+\frac{4\pi N_i}{|\mathbf{q}+\mathbf{G}|^2}\mathbf{p}_0(\mathbf{q}+\mathbf{G},\omega)\cdot\mathbf{E}_0. \tag{9}$$

The last term accounts for the dipolar fields of the ion cores; N_i is the ion density and $\mathbf{p}_0(\mathbf{q},\omega)$ is the Fourier transform of the core polarization. To close the equations we note that the local field $\mathbf{E}_0$ is related to the total field, and hence the potential, by

$$\mathbf{E}_0=-\sum_{\mathbf{G}} i(\mathbf{q}+\mathbf{G})\phi_{\mathbf{G}}^{\text{tot}}(\mathbf{q},\omega)/[1-\beta(\omega)]. \tag{10}$$

The denominator compensates for the "self-field" explicitly treated in (7).

Equation (9) is finally solved in the $q\to 0$ limit with one further approximation motivated by the fact that the valence electrons in simple metals have a free-particle-like dispersion. That is, we take $\chi_v^0(\mathbf{G},\mathbf{G}',\omega)\approx\delta_{\mathbf{G},\mathbf{G}'}\chi_v^0(\mathbf{G},\omega)$, which therefore neglects local field effects with respect to the valence-electron response. Local field effects with regard to the core electrons, however, are included completely as evidenced by the fact that the total potential contains nonzero–wave-vector components. The solution of (9) and (10) finally yields

$$\epsilon(\omega)=1-\lim_{q\to 0}\frac{4\pi}{q^2}\chi_v^0(\mathbf{q},\omega)+\frac{4\pi N_i\alpha(\omega)}{1-\frac{4}{3}\pi N_i\alpha(\omega)\{1+\sum_{\mathbf{G}\neq 0}f(\mathbf{G},\omega)[1-1/\epsilon_v(G,\omega)]\}}, \tag{11}$$

with

$$\epsilon_v(G,\omega)=1-(4\pi/G^2)\chi_v^0(G,\omega) \tag{12}$$

and

$$f(G,\omega)=[p_0(G,\omega)/G]/[p_0(G,\omega)/G]_{G=0}. \tag{13}$$

Apart from the appearance of the "form factor" $f(G,\omega)$, which arises because of the extended spatial distribution of the core polarization, the result in (11) is very similar to that obtained earlier within a point-dipole model.[7] The final term in (11) illustrates the modification of the CM expression due to core-valence interactions.

The main advantage of the present formulation is that a precise definition of the core polarizability $\alpha(\omega)$ is provided by the solution of (7). The core response function χ_a^0 appearing in this equation can be calculated by use of methods described elsewhere[3]; however, its form differs from that of the free ion. Since it represents an ion in a metallic host, excitations to the occupied valence states must be excluded. The potential determining the core states was obtained by performing a self-consistent screening calculation for a single ion at the center of a vacancy in a jellium host having a density equal to that of the valence electrons. Of course with neglect of the Bloch character of the final states, the characteristic extended x-ray-absorption fine structure observed with core excitations is not reproduced. To the extent that the ionic potentials scatter the valence electrons weakly, this is not an important limitation.

In Fig. 1 we show the dynamic polarizability for In as obtained from Eqs. (7) and (8). $\text{Im}\alpha(\omega)$ is of

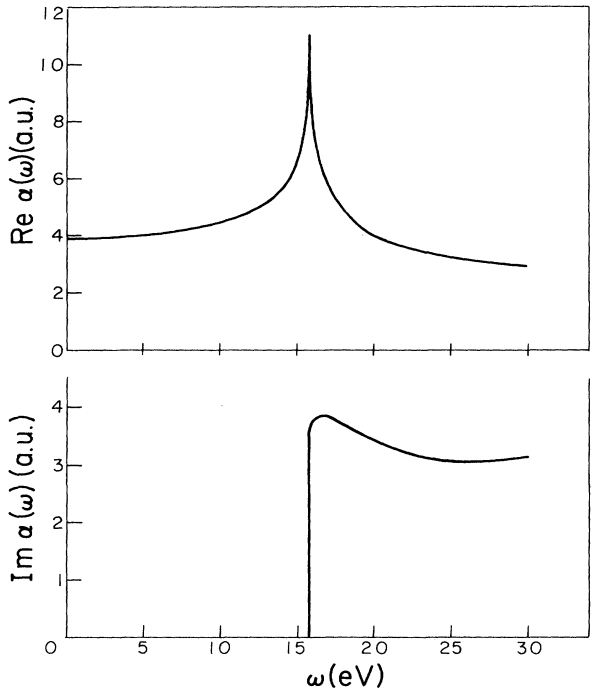

FIG. 1. Real and imaginary parts of the core polarizability of In vs frequency, in electronvolts.

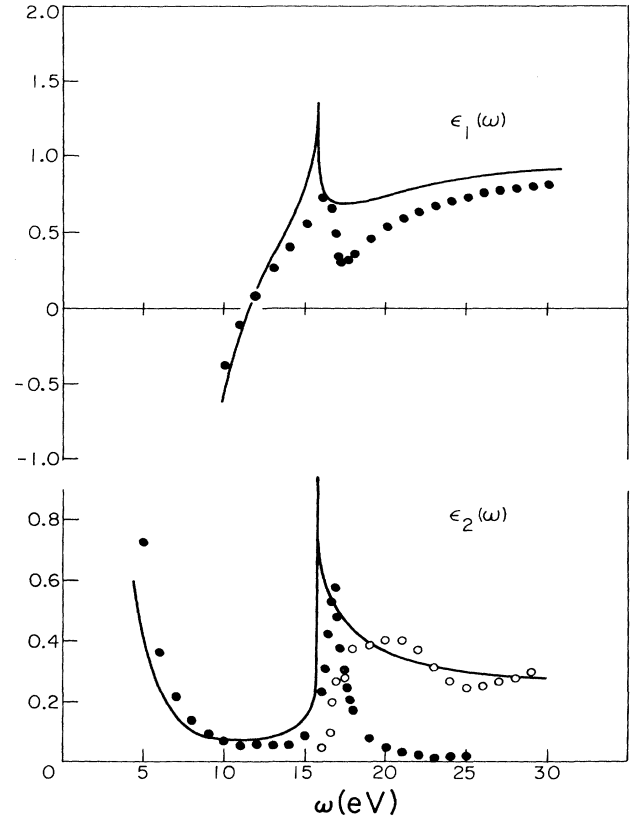

FIG. 2. Theoretical and experimental dielectric function of In vs frequency [solid line, theory; closed circles, Krane (Ref. 9); open circles, Jezequel, Thomas, and Lemonnier (Ref. 10)].

course zero for $\omega \leq \epsilon_F$, and as a result the real part of $\alpha(\omega)$ exhibits a logarithmic singularity at the Fermi energy. This divergence has an important effect on $\epsilon(\omega)$ because of the denominator in the CM term. It is clear from the figure that a Lorentz-oscillator model of the polarizability used previously for this problem is not adequate.[7]

To complete the evaluation of $\epsilon(\omega)$, the valence susceptibility $\chi_v^0(\mathbf{G}=\mathbf{G}'=0,\omega)$ is required. This quantity has contributions of two types: (i) an intraband term which contributes $(\omega_p^0/\omega)^2 m/m_{\rm opt}$, where $m_{\rm opt}$ is the optical mass, and (ii) an interband contribution which has an extended spectral distribution above the lowest band-gap energy. The interband spectral density was modeled by various analytic expressions suggested by pseudopotential calculations,[8] but the final results for $\epsilon_1(\omega)$ do not depend sensitively on the choice provided that the requirements of the f-sum rule are fulfilled. Since χ_v^0 by definition includes excitations from the valence bands to unoccupied states, its f-sum rule gives an effective valence-electron density $n_{\rm eff}$ which is enhanced above the free-electron value n_0.[1] The enhancement can be estimated by calculating the dipole matrix elements between the core and valence states within the same model used to construct χ_a^0. In the vicinity of the plasma frequency it was found that $\mathrm{Re}(4\pi/q^2)\chi_v^0$ could be well represented by its high-frequency limit, $(\omega_p^*/\omega)^2$. The effective plasma frequency defined by $(\omega_p^*/\omega_p^0)^2 = n_{\rm eff}/n_0$ is given in Table I for each of the metals considered.

The calculated real and imaginary parts of $\epsilon(\omega)$ are shown for the example of In in Fig. 2. The results for Cd and Sn are qualitatively similar. In the vicinity of the $4d$ threshold, $\epsilon_2(\omega)$ is dominated by the CM term and exhibits a distinctive asymmetric profile. The sharp peak at threshold is a consequence of the LFE accounted for by the denominator of the CM term; in their absence, $\epsilon_2(\omega)$ would appear similar to $\mathrm{Im}\alpha(\omega)$ illustrated in Fig. 1. Before comparing these results with experiment, however, we should mention that the theoretical profile will be modified by two effects: (i) the actual finite width of the core d band and (ii) its spin-orbit splitting.[11] Both of these effects will broaden the profile and hence reduce the pronounced structure.

Two sets of experimental data are shown in Fig. 2. One (solid points) is derived from a Kramers-Kronig analysis of the electron-energy-loss spectrum as measured in a limited range of energies.[9] It clearly exhibits a peaking in $\epsilon_2(\omega)$ at threshold, but falls off more rapidly at higher frequencies than would be expected for excitation of an atomic level. The other

data set[10] is obtained directly from the measured optical conductivity and, apart from the absence of a sharp peak at threshold, is in overall good agreement with the calculated spectral density. The structure in $\epsilon_1(\omega)$ is also in reasonable accord with experiment. The peak is essentially a result of the logarithmic singularity in $\mathrm{Re}\alpha(\omega)$ and its asymmetry is due to the sudden rise in $\mathrm{Im}\alpha(\omega)$ above threshold. In view of the differences between the two sets of data for $\epsilon_2(\omega)$, a more definitive experimental study would be desirable. Nevertheless, it is clear that the theory is qualitatively correct in the region of the $4d$ threshold.

The positive contribution to $\epsilon_1(\omega)$ from the CM term is the source of the significant downward shift of the plasma frequency [determined by $\epsilon_1(\omega_p)=0$] from its free-electron value. The calculated values of ω_p are given in Table I and are seen to agree very well with experiment. It is important to note that this agreement is achieved with two competing effects: an upward shift of the plasma frequency due to enhancement of the valence-electron transition matrix elements and a downward shift due to the screening of the macroscopic field provided by core polarization.

In conclusion, we have demonstrated that core polarization in metals has important implications even for relatively simple metals and, specifically, that a careful treatment of these effects leads to a quantitative explanation of the observed plasma frequencies.

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[a]Permanent address: Department of Physics, Queen's University, Kingston, Ontario K7L 3N6, Canada.

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