Electron energy loss spectroscopy in metallic indium

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Measurements of the energy loss spectra of fast (30 keV) electrons in indium have been made. A strong plasma resonance at an energy of 11.22 eV dominates the spectra obtained. The breadth of this resonance at half height (corrected for the instrumental function) is 0.30 eV, which is the record low value for all materials except *K* and possibly Na. Low-intensity threshold singularities are also observed in the spectra, the positions of which correlate well with the binding energy of the $4d_{5/2}$ and $4d_{3/2}$ core electrons, so that we can suggest that they correspond to these core levels. These features are well reproduced by theoretical calculations taking into account the polarization of the 4*d* levels of indium, although the intensity of the threshold features in the calculated spectrum is appreciably greater than the corresponding experimental magnitude. A theoretical calculation of the dielectric function and the loss function in In was carried out within the pseudopotential framework using a local Heine–Abarenkov model potential, the parameters of which were varied. It is shown that the pseudopotential approach correctly describes the width of the plasma resonance in indium, but cannot explain the plasmon energy shift compared with the magnitude of $\hbar\omega_p$ equal to 12.62 eV. This shift should probably be associated with the influence of the polarization of the 4*d* core level electrons, although the polarizability of these levels is extremely small, which is indicated by the low intensity of the threshold features corresponding to such a polarization.

1. INTRODUCTION

Electron energy loss spectroscopy (ELS) is designed for the study of the electronic structure of solids and provides information about plasma oscillations and interband transitions, about the binding energy of electrons within the ion cores and their polarizability, and also about the general nature of the dependence of the macroscopic dielectric function $\varepsilon_m(\mathbf{q},\omega)$ of the medium on wave vector and frequency. All this information is extracted from the double differential scattering cross section for fast electrons when they traverse a thin film, and is determined by the expression

$$\frac{d^2\sigma}{d(\hbar\omega)d\Omega_{\mathbf{q}}}=-\frac{\Omega}{(\pi e a_B q)^2}\,\mathrm{Im}\,\varepsilon_M^{-1}(\mathbf{q},\omega), \tag{1}$$

where $\hbar\omega$ and $\hbar\mathbf{q}$ are the energy and momentum lost by the electron in the scattering process, e is the electronic charge, a_B is the Bohr radius and Ω is the active volume of the specimen, equal to its thickness multiplied by the cross-sectional area of the electron beam.

The so-called *f*-sum rule applies to the first moment in frequency of the function $\mathrm{Im}\,\varepsilon_m^{-1}(\mathbf{q},\omega)$

$$-\frac{2}{\pi}\int_0^\infty d\omega\,\omega\,\mathrm{Im}\,\varepsilon_M^{-1}(\mathbf{q},\omega)=\omega_p^2, \tag{2}$$

where ω_p is the classical plasma oscillation frequency

$$\omega_p=\sqrt{4\pi n_0 e^2/m} \tag{3}$$

determined by the density n of valence electrons and their mass m. It is easy to see from Eqs. (1) and (2) that the greatest contribution to the cross section comes from inelastic processes in which electrons lose an energy of the order of $\hbar\omega_p$.

This circumstance is very clearly manifest in experimental spectra for simple metals in the form of an intense and rather narrow peak, positioned at an energy E_p, corresponding approximately to $\hbar\omega_p$. This peak corresponds to the creation of a well-defined elementary excitation in the electron subsystem, called a plasmon. The energy of the plasmon is found from the dispersion relation

$$\mathrm{Re}\,\varepsilon_M(\mathbf{q},\omega)=0, \tag{4}$$

which determines the frequency $E_p(\mathbf{q})/\hbar$ dependent on $\mathbf{q}$, of which the real part of the dielectric function $\varepsilon_M(\mathbf{q},\omega)$ becomes zero.

A much greater width and, consequently, also a less intense plasma resonance is observed in semiconductors than in simple metals. Such a resonance has a complicated structure in transition metals and is a superposition of two or more peaks. Finally, in oxides and in other dielectrics the energy loss spectra are usually very spread-out peaks, the positions and widths of which are comparable to $\hbar\omega_p$.

There is a small combined contribution to part of the remaining features in the spectra (interband transitions etc.) and in the majority of cases their intensity is relatively small, which hinders detailed study. Therefore, in most work on ELS the main effort has been directed toward

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studying plasma oscillations. However, the gradual improvement in experimental equipment and methods has made it possible to turn to studies of other excitations as well, appearing less clearly in the spectra.

In particular, the study of effects associated with the excitation of the ion cores is one of the interesting developments. The corresponding resonances usually appear as an absorption edge with characteristic fine structure determined by the density distribution of states above the Fermi level. Such absorption edges are observed in the energy range from several tenths of electron volts to several kiloelectron volts and their positions are determined by the binding energy of the ion cores.

In some materials the binding energies of the upper core levels are fairly close to the plasma oscillation energies. In that case strong polarizability arises both in conduction band electrons and for electrons of these core levels at frequencies near the plasma resonance. Interesting effects can then be observred, associated with interactions of these two types of electrons and also with polarization of the ion cores themselves (see, for example, Refs. 1, 2).

One of the substances in which this situation is realized is metallic indium, in which the bound $4d_{5/2}$ and $4d_{3/2}$ outer core states closest to the valence band lie at (16.74 and 17.64 eV)[3] (16.40 and 17.26 eV)[4] below the Fermi level respectively, which differs only insignificantly from the classical energy of plasma oscillations in indium equal to $\hbar\omega_p = 12.62$ eV. Indium is a simple metal with a tetragonal face-centered lattice ($a = 4.585$ Å $c = 4.941$ Å). The atomic ground state configuration of indium is $[Kr]4d^{10}5s^25p^1$.

ELS studies in indium have been carried out by a whole series of workers.[5–9] In spectra measured by them an intense plasma peak is dominant, the position and width (at half-height) of which varies among the different authors from 11.4 to 12.3 eV and from 0.39 to 0.7 eV, respectively. There are also weak lines in the spectra associated with surface plasma oscillations and multiple excitations of bulk plasmons, and also by partial oxidation of the metal films studied. Other features were not generally observed.

However, in unpublished work (a spectrum from it is shown in Ref. 10) an additional peak was observed in the ELS for indium, corresponding roughly with the excitation energies of the 4*d* core levels in the material. The existence of such a peak was described by Sturm[10] and later by Sturm *et al.*[11] as a collective resonance of the system of polarized ion cores. The calculation of the loss function was carried out within the random phase approximation framework, taking account of the mutual interaction between charge fluctuations of the conduction electrons and ion cores. Using the simple expression for a Lorentz oscillator to describe the polarization of the 4*d* electrons,[10] the corresponding resonance (below we call it a polarization resonance) in the calculated spectrum was about three times as intense as the analogous feature observed experimentally and was described by a curve similar to a Lorentz distribution. However, the inclusion of an exact expression for the polarizability of ion cores in metals[11] led to an

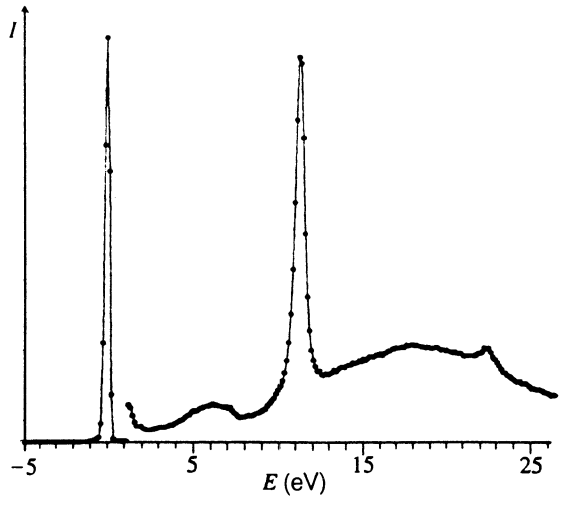

FIG. 1. Electron energy loss spectrum of In in the energy range from–5 to 26.5 eV measured at zero scattering angle.

appreciable reduction in the relative amplitude of the polarization resonance (more than by a factor of two) and to a change in its shape from a "Lorentzian distribution" to an "absorption edge" (threshold singularity). In this way the results of theoretical calculation and the experimental results disagree as to both amplitude and shape of the polarization resonance. In this situation we considered it advisable to return once more to a detailed experimental and theoretical study of ELS in metallic indium. The results of this investigation are presented in the present work.

2. EXPERIMENTAL RESULTS

The ELS measurements were made with the apparatus described earlier by Zharnikov *et al.*[12] The energy resolution and momentum transfer reached 0.15 eV and 0.05 $Å^{-1}$ (5×10^{-4} rad), respectively, with the initial beam energy 30 keV. Thin film indium specimens were deposited by thermal deposition in a vacuum of 10^{-6} torr onto collodion support films cooled with liquid nitrogen. The thickness of the specimens was 300–450 Å.

A typical ELS spectrum for metallic indium measured at zero scattering angle is shown in Fig. 1. The narrow peak at 11.2 eV dominates, evidently corresponding to excitation of a bulk plasmon in the indium conduction band electron system; a double excitation process is responsible for the resonance at 22.5 eV, while the weak feature in the vicinity of 6 eV is probably associated with a surface plasmon. The latter is confirmed by spectra taken at a nonzero scattering angle (Fig. 2). In these spectra the relatively intense feature near 6 eV decreases with increasing scattering angle appreciably faster than the analogous feature for a bulk plasmon, as it should for surface excitation. The surface plasmon energy for a metallic indium film with a clean surface, in vacuo, should be $E_p/\sqrt{2} \cong 7.9$ eV. However, in our case one of the surfaces of the film is in firm contact with the collodion substrate while the second may be covered with some indium oxide layer which leads to a

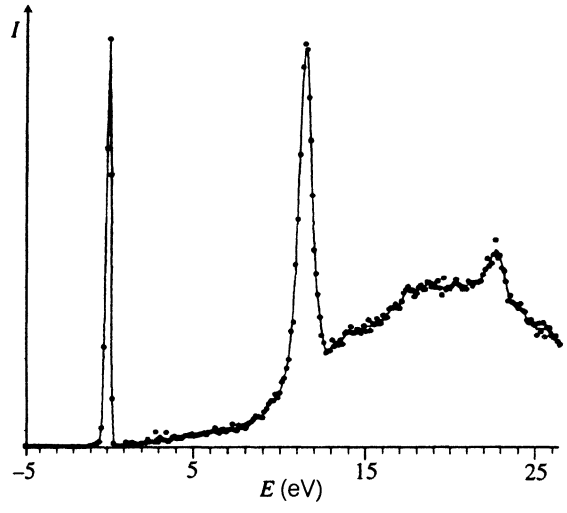

FIG. 2. Electron energy loss spectrum of In in the energy range from–5 to 26.5 eV measured at nonzero scattering angles (q=0.15 Å).

reduction in the surface plasmon energy. The effect of these dielectric films appears in the form of a broad hump lying in the energy region between the single and double plasmon peaks. No intense resonance is observed in the spectra shown in Fig. 1 in the region of the excitation of the 4*d* core levels.

In order to study this section of the spectrum in more detail additional ELS measurements were made in the energy range 15.5–19.5 eV. The corresponding spectrum is shown in Fig. 3, where the arrows also show the binding energies of the $4d_{5/2}$ and $4d_{3/2}$ core levels, according to Poole *et al.*[4] As can be seen from Fig. 3, the points of inflection are quite clearly observed in the experimental spectrum at these energies at which increased energy losses occur. It can be concluded from such agreement that these points reflect thresholds for interband transitions with excitation of $4d_{5/2}$ and $4d_{3/2}$ electron core levels in unfilled

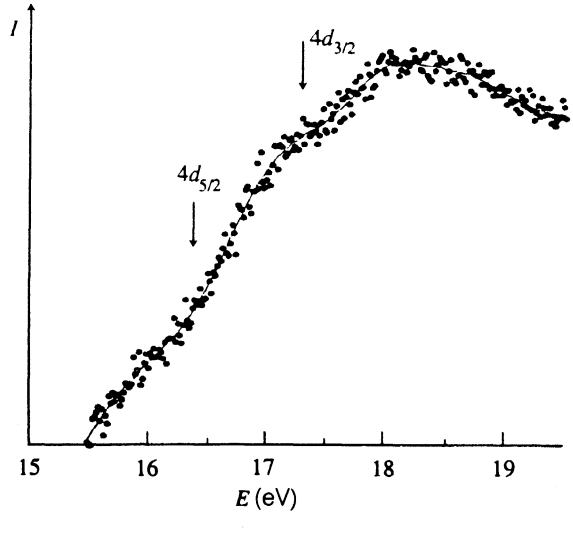

FIG. 3. Electron energy loss spectrum of In in the energy range from 15.5 to 19.5 eV measured at zero scattering angle.

states above the Fermi surface. The intensity of these threshold features is extremely small and they are practically invisible in the spectrum of Fig. 1, taken in the same energy range with lower statistics. A possible explanation of the low intensity of the observed transition is that near the Fermi level *s*-type states predominate, transitions from which to *d*-levels are forbidden by the *l* quantum number selection rules (changes $\Delta l=0, \pm 1$).

Comparison of Figs. 1 and 3 with the experimental spectrum given by Sturm[10] suggests that the broad low-intensity peak near 17 eV we also observed was taken as the feature associated with the excitation of 4*d* core level electrons. The exact shape of this peak and the appearance of finer features on it were not considered there.

Since polarization of the 4*d* levels in indium should have an effect on the position and width of the plasma resonance, it is interesting to analyze the experimental results from this point of view. From the results of analysis of nine spectra taken on different specimens, the position of this resonance corresponds to an energy $E_p=11.22\pm0.02$ eV and its width at half height $\Delta E_{1/2}$ (correcting for the instrumental function) is 0.30 ± 0.02 eV.

Comparison of the values of E_p and $\hbar\omega_p$ shows that the energy of a bulk plasmon in the conduction electron system of indium is lower than the energy of plasma oscillations for a homogeneous electron gas of the same density. However, at the same time the value of E_p we found is in good agreement with the results of previous measurements.[6–9] The plasma resonance itself is extremely narrow: the value of $\Delta E_{1/2}$ for indium is smaller than the analogous value for all materials studied earlier except potassium (0.2–0.3 eV[13]) and possibly sodium (0.25–0.4 eV[13]). The higher values of the halfwidth of the plasma peak in indium observed earlier may be attributed to specimens of insufficiently high quality and low energy resolution of the apparatus.

3. THEORETICAL ANALYSIS OF RESULTS

A theoretical description of plasma excitation in indium cannot, unfortunately be given within the framework of a relatively simple model of a homogeneous electron gas, since such an approach leads to the conclusion that in the energy loss spectrum for zero momentum transfer $\mathbf{q}$ a δ-function singularity should be observed at ω_p (12.62 eV). The existence of this singularity, i.e., the absence of damping for the plasmon, is associated with the fact that in the homogeneous electron gas model the energy and momentum conservation laws for the decay of a plasmon into an electron–hole pair are only satisfied over a certain range of values of ω and q, the so-called Landau continuum. Since the point ($\omega=\omega_p$, $q=0$) does not fall in this continuum, the decay of a plasmon into an electron–hole pair is forbidden and, consequently, damping is absent. However, such a decay becomes possible if the crystal lattice takes part in the process. It takes up part of the momentum and enables the conservation laws to be satisfied. In other words, for any ω and q a reciprocal lattice vector $\mathbf{G}$ can be selected such that the point ω, $\mathbf{q}+\mathbf{G}$ falls in the Landau continuum.

Taking account of the crystalline structure of a material requires calling on the formalism of the dielectric matrix

$$\varepsilon(\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}',\omega)\equiv\hat{\varepsilon}_{\mathbf{G}\mathbf{G}'}(\mathbf{k},\omega), \tag{5}$$

describing the shielding properties of the electron subsystem of a real crystal. This matrix is defined in the vector space, of macroscopically large dimensionality, of the reciprocal lattice $\{\mathbf{G}\}$. Here and later $\mathbf{k}$ is a wave vector lying within the boundaries of the first Brillouin zone.

The calculation of its dielectric matrix for a known electron band structure of a metal, although it runs to a sizable numerical problem, is not associated with fundamental difficulties (at least within the approach of the most widely used random phase approximation). The first expressions for the dielectric matrix in this approximation were obtained by Adler[14] and by Wiser[15]

$$\varepsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{k},\omega)=\delta_{\mathbf{k}+\mathbf{G}\cdot\mathbf{k}+\mathbf{G}'}-2v(\mathbf{k}+\mathbf{G})\sum_{\lambda\lambda'}\frac{n_\lambda-n_{\lambda'}}{\hbar\omega-E_{\lambda'}-E_\lambda+i\delta}\times\langle\lambda|\exp[-i(\mathbf{k}+\mathbf{G})\mathbf{r}]|\lambda'\rangle\times\langle\lambda'|\exp[i(\mathbf{k}+\mathbf{G}')\mathbf{r}]|\lambda\rangle. \tag{6}$$

In this expression λ and λ' indicate the single-particle Bloch states corresponding to energies E_λ and $E_{\lambda'}$ and the Fermi occupation functions n_λ and $n_{\lambda'}$, $\delta_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'}$ is the Dirac delta function, while $v(\mathbf{q})=4\pi e^2/q^2$ is the Fourier component of the Coulomb interaction.

To recover the form of the energy loss spectrum, it is necessary to invert the dielectric matrix, since the loss function $L(\mathbf{q},\omega)$ for a real crystal describing such a spectrum is determined by the relation

$$L(\mathbf{q},\omega)=\mathrm{Im}\,\hat{\varepsilon}^{-1}_{\mathbf{G}\mathbf{G}}(\mathbf{k},\omega), \tag{7}$$

where $\mathbf{q}=\mathbf{k}+\mathbf{G}$ and the corresponding diagonal element of the inverse matrix with respect to Eq. (5) also occurs. The problem of such an inversion has not so far been solved for the general case.

However, in simple metals where the pseudopotential of the electron–ion interaction $V(\mathbf{r})$ is weak and an analytic inversion of the dielectric matrix can be carried out within perturbation theory, a relatively simple expression can be obtained for the loss function of a real crystal with an accuracy up to second order in $V(\mathbf{r})$. The corresponding theory was developed by Wiser.[15] In the limiting case $q\to 0$, the expression takes the form

$$L(\omega)=\lim_{\mathbf{q}\to 0}\left[\frac{\varepsilon_2(\mathbf{q},\omega)}{\varepsilon_1^2(\mathbf{q},\omega)+\varepsilon_2^2(\mathbf{q},\omega)}\right], \tag{8}$$

where $\varepsilon_1(\mathbf{q},\omega)$ and $\varepsilon_2(\mathbf{q},\omega)$ are the real and imaginary parts of the so-called macroscopic dielectric function $\varepsilon_M(\mathbf{q},\omega)$, which for small $\mathbf{q}$ gives the equation

$$\varepsilon_M(\mathbf{q},\omega)|_{\mathbf{q}\to 0}=1-\frac{\omega_p^2}{\omega^2}-\frac{1}{m^2\omega^2}\sum_{\mathbf{G}\neq 0}\frac{(\mathbf{q}\mathbf{G})^2}{q^2G^2}|G^2V_L(\mathbf{G})|^2\times\left[\frac{1}{\varepsilon(\mathbf{G},\omega)}-\frac{1}{\varepsilon(\mathbf{G},0)}\right], \tag{9}$$

where $\varepsilon(\mathbf{G},\omega)$ is the dielectric function of a homogeneous electron gas of the same density.

The Fourier component of the lattice potential is denoted by $V_L(\mathbf{G})$. This quantity can be represented in the following way

$$V_L(\mathbf{G})=N_\alpha V(\mathbf{G})S(\mathbf{G}), \tag{10}$$

where N_a is the total number of atoms, $V(\mathbf{G})$ is the form factor of the electron–ion interaction pseudopotential, and

$$S(\mathbf{G})=\frac{1}{\nu}\sum_{s=1}^{\nu}\exp(-i\mathbf{G}\rho_s) \tag{11}$$

is the structure factor. The radius vector of the sth atom and the total number of atoms in the elementary cell are denoted by $\boldsymbol{\rho}_s$ and ν respectively.

We carried out calculations of the macroscopic dielectric function (Eq. 9) and the loss function (Eq. 8) for indium in the region close to the plasma resonance. For this we used a local Heine–Abarenkov model potential

$$V(r)=\begin{cases}uZe^2/R_c, & r\leqslant R_c\\ -Ze^2/r, & r>R_c\end{cases}, \tag{12}$$

and the random phase approximation for the dielectric function of a homogeneous electron gas. The magnitude of $S(\mathbf{G})$ was made equal to unity by using an appropriate choice of radius vectors. The quantity Z in Eq. (12) was taken as 3, and the values of the parameters u and R_c were taken from Sturm,[17] where they were determined by fitting the Fermi surface of indium. u was then assumed equal to zero (Ashcroft empty core model) and two possible choices were obtained for R_c: $R_c=0.575$ Å and $R_c=0.715$ Å.

The function $\varepsilon_M(\mathbf{q},\omega)$—and thus $L(\mathbf{q},\omega)$—can be directly seen from Eq. (9) to be independent of the absolute magnitude of the wave vector in the limit $\mathbf{q}\to 0$, but because of the presence of the scalar product $\mathbf{q}\mathbf{G}$ under the summation sign, there is a dependence on the direction of $\mathbf{q}$ relative to some assigned axis (for non-cubic lattice symmetries). Taking into account that polycrystalline indium specimens were studied in our experiments, the appropriate averaging of the function $L(\mathbf{q},\omega)$ calculated by Eq. (8) must be carried out over all possible directions of the vector $\mathbf{q}$. For this the following integral must be evaluated

$$\bar{L}(\omega)=-\frac{1}{2}\mathrm{Im}\int_0^\pi\frac{d\theta}{\varepsilon_\omega(\theta)}. \tag{13}$$

Here the macroscopic dielectric susceptibility is expressed in terms of $\varepsilon_\omega(\theta)$ as a function of θ, the angle between some preferred axis and the vector $\mathbf{q}$. For systems possessing a symmetry axis, this function takes the form

$$\varepsilon_\omega(\theta)=1-\omega_p^2/\omega^2-(\omega_p^4/\omega^4)(a+b\cos^2\theta),$$

or

$$\varepsilon_\omega(\theta)=c_1-c_2\cos^2\theta, \tag{14}$$

where a, b, c_1 and c_2 are the complex frequency functions, the values of which have also been calculated.

A summation over 125 coordination spheres went into the calculation procedure directly, which included 1474 nonzero reciprocal lattice vectors for 200 frequency values in the region of the plasma resonance, according to the following formula, which can be obtained from Eq. (9)

$$\varepsilon_M(\mathbf{q},\omega)\big|_{\mathbf{q}\to 0}=1-\frac{\omega_p^2}{\omega^2}-\frac{\omega_p^4}{\omega^4} \times \sum_{\mathbf{G}\neq 0}\cos^2\alpha_{\mathbf{qG}}W_G^2\left[\frac{1}{\varepsilon(\mathbf{G},\omega)}-\frac{1}{\varepsilon(\mathbf{G},0)}\right]. \tag{15}$$

Here $\alpha_{\mathbf{qG}}$ is the angle between the vectors $\mathbf{q}$ and $\mathbf{G}$, the coordinates of which are defined in a rectangular coordinate system; the z axis coincided with the lattice c axis. Then $\mathbf{q}=(q\sin\vartheta/\sqrt{2},\ q\sin\vartheta\sqrt{2},\ q\cos\vartheta)$, where ϑ is the angle between the z axis and the vector $\mathbf{q}$ (the azimuthal angle ϕ is taken to be 45° in view of the lattice symmetry). The quantity W_G is given by

$$W_G=(1+u)\cos(GR_c)-u\frac{\sin(GR_c)}{GR_c}$$

(see Eq. (12)).

The summation in Eq. (15) for each value of frequency was carried out for two values of the angle θ, 0 and $\pi/2$, so that the coefficients c_1 and c_2 in Eq. (14) could then be calculated. Using these values, it is easy to carry out the integration in Eq. (13), which leads to the expression

$$\bar{L}=\frac{1}{2}\,\mathrm{Im}\,\frac{1}{\sqrt{c_1c_2}}\ln\left|\frac{\sqrt{c_1}-\sqrt{c_2}}{\sqrt{c_1}+\sqrt{c_2}}\right|,$$

which can then be used for a numerical calculation. A similar procedure for evaluating the loss function in polycrystalline specimens was used by Gorobchenko *et al.*[1] as applied to Cd and Zn.

The curve obtained for the loss function for a polycrystalline indium specimen has the form of a resonance peak, the shape of which is close to Lorentzian, and the position and full width at half maximum the two sets of parameters of the model potential of Eq. (12), indicated above, are

$$(1)\ u=0,\quad R_c=0.575\ \text{Å}\begin{cases}E_p=12.38\ \text{eV},\\ \Delta E_{1/2}=0.32\ \text{eV},\end{cases} \tag{16a}$$

$$(2)\ u=0,\quad R_c=0.715\ \text{Å}\begin{cases}E_p=12.05\ \text{eV},\\ \Delta E_{1/2}=0.51\ \text{eV}.\end{cases} \tag{16b}$$

A comparison of the experimental data and the results of the theoretical calculation (Eq. 16) shows that for these two choices of parameters there is an appreciable discrepancy between the calculated and observed plasmon energy.

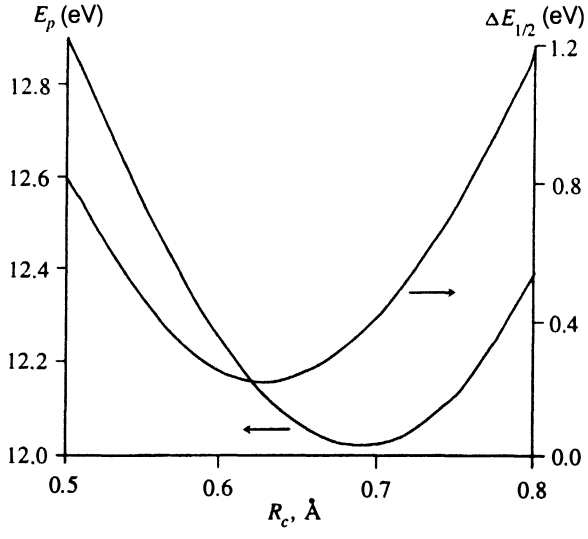

FIG. 4. $E_p(R_c)$ and $\Delta E_{1/2}(R_c)$ for In calculated using a Heine–Abarenkov local model potential, in the empty core model ($u=0$).

At the same time, the theoretical value of $\Delta E_{1/2}$ for the first set agrees significantly better with the corresponding experimental value.

If we stay with the Ashcroft empty core model ($u=0$), the $E_p(R_c)$ and $\Delta E_{1/2}(R_c)$ dependences are as shown in Fig. 4, and in this case the experimentally determined width of the plasma resonance $\Delta E_{1/2}=0.30\pm0.02$ eV can be obtained from the calculations for $R_c=0.674\pm0.006$ Å. The theoretical position of the plasma resonance is then equal to $E_p=12.035\pm0.005$ eV, which considerably exceeds the corresponding experimental value. The latter also occurs for the minimum value E_p 12.029 eV, which is obtained for $R_c=0.690$ Å ($\Delta E_{1/2}=0.389$ eV).

The next step was an attempt to choose both parameters of the pseudopotential (Eq. 12) to satisfy the values of the width and the position of the plasma peak simulta-

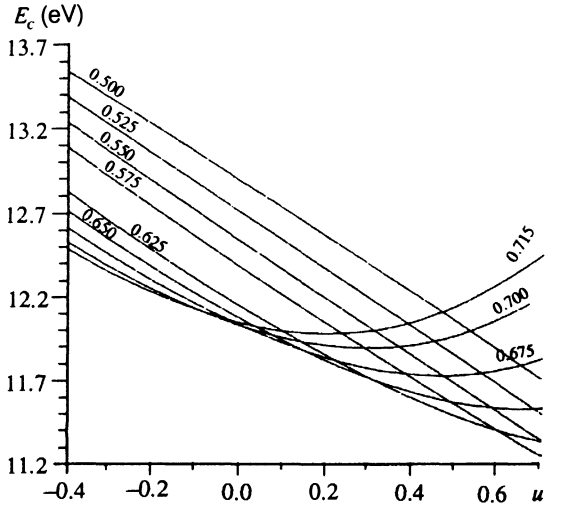

FIG. 5. The $E_p(u)$ dependence for In calculated for various values of the parameter R_c (the numbers next to the curves are values of R_c in Å).

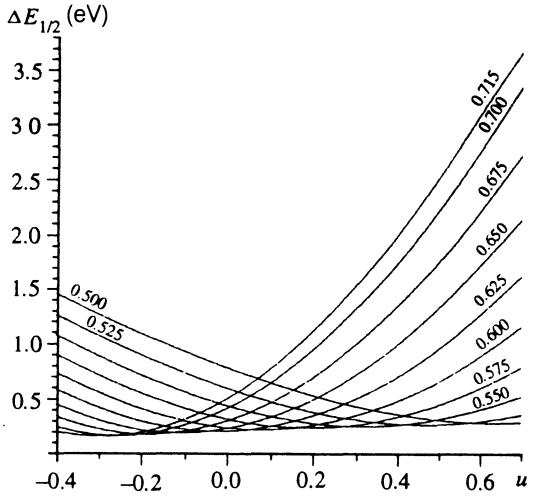

FIG. 6. The $E_{1/2}(u)$ dependence for In, calculated for various values of the parameter R_c (the numbers next to the curves are values of R_c in Å).

neously. Then, in order for the pseudopotential to still be considered small, the maximum value of the absolute value of the parameter u should be of the order of unity. In the calculations, u varied from–0.4 to 1, while the parameter R_c varied from 0.500 Å to 0.715 Å. The curves obtained for $E_p(u)$ and $\Delta E_{1/2}(u)$ for ten different values of the parameter R_c in this interval are shown in Figs. 5 and 6 respectively. Analysis of these curves leads to the conclusion that simultaneous satisfaction of the two conditions—the position and width of the plasma resonance—is probably impossible, even when using clearly nonphysical values of the parameters of the pseudopotential (Eq. 12). The positions of the resonance corresponding to those found experimentally thus correspond to values of the peak width greater than the experimental value, and vice versa.

Taking account of the real crystal structure (within the pseudopotential approach) is thus not completely sufficient for a correct description of the plasma resonance found in this metal. This is confirmed by the fact that it is essential to include other mechanisms in the consideration, which have an effect on the parameters of this resonance. The most important of these is the polarization of the 4*d* ion core levels. The existence of this polarization or, in other words, the interaction between plasma oscillations of the conduction electrons and the polarized 4*d* ion cores must lead to both a lowering of the energy of these oscillations and a reduction in their lifetime (broadening of the corresponding peak) due to an additional damping mechanism. It should, however, be noted that the experimental value of $\Delta E_{1/2}$ is well reproduced within the pseudopotential approach for a whole range of parameters u and R_c and, in particular by using one of the pairs of parameters obtained by Sturm.[17] In any particular case, the minimum values of $\Delta E_{1/2}$ are obtained for various parameters R_c exceeding 0.17 eV, and mainly occupy the interval 0.2–0.3 (see Fig. 6 and Table I).

It can thus be concluded that inclusion of the crystal structure of indium in the discussion is sufficient in actual practice to reproduce the experimental plasma peak width. The main decay channel of a plasmon in indium can be explained in the same way, namely through the creation of electron–hole pairs in the conduction band when umklapp processes take part.

Regarding the plasmon energy, there is an appreciable discrepancy between the calculated and experimental values. As is seen from Fig. 5, the small values of this quantity compared with the results of measurements can, in principle, be obtained for relatively large values of the parameter u. However, as can be seen in Fig. 6, these values correspond to values of $\Delta E_{1/2}$ that are clearly nonphysical, and too high, since the inclusion of other factors (apart from crystal structure) can only lead to a broadening of the plasma peak and not to its narrowing. The values of E_p corresponding to the experimentally observed values lie in the range from 12.1 to 12.5 eV. The additional polarization which an electron gas undergoes due to electron–ion interaction thus does not achieve the necessary lowering of the energy of plasma oscillations. This lowering can, however, be achieved through interaction between these oscillations and polarized 4*d* cores, similar to that realized in metallic cadmium.[1,2] However, as shown in the present work, the intensity of polarized resonances in indium is very small, indicating that the polarizability of the 4*d* levels is fairly weak, so that it is still an open question whether it can be responsible for the total value of the observed shift of the

TABLE I. Minimum values of the width $\Delta E_{1/2}^{\min}$ of the calculated plasma resonance as a function of u dependent on the parameter R_c and the position of the peak $E_p^{\min}$ corresponding to these values.

R_c, Å	u_{min}	$\Delta E_{1/2}^{min}$ (eV)	E_p^{min} (eV)
0.715	-0.295	0.168	12.338
0.700	-0.255	0.175	12.313
0.675	-0.185	0.187	12.273
0.650	-0.110	0.201	12.232
0.625	-0.015	0.214	12.170
0.600	0.080	0.228	12.170
0.575	0.190	0.242	12.061
0.550	0.320	0.257	11.988
0.525	0.470	0.272	11.905
0.500	0.635	0.286	11.824
0.400	1.680	0.338	11.365

plasma resonance in indium (minus the insignificant shift due to electron–ion interaction).

4. CONCLUSION

It has been established as a result of investigations of electron energy loss spectra in metallic indium that the metal has a weak polarizability of the $4d_{3/2}$ and $4d_{5/2}$ ion core levels. The core electron excitation in the spectra obtained correspond to threshold-type features of extremely low intensity. The dominant feature in these spectra is a bulk plasma resonance with smaller width than similar peaks in other elements, except for K and possibly Na. This resonance shifts by ≈ 1.4 eV in the direction of lower energies compared with the classical energy of plasma oscillations in indium. The shape of the resonance is well reproduced using a theoretical analysis of the dielectric function of In in the framework of pseudopotential theory using a model Heine–Abarenkov local potential, which suggests a decisive role for Umklapp processes in the damping of plasma oscillations. At the same time, the calculated magnitude of the shift in the plasma resonance due to additional polarizability which the electron gas acquires in the presence of electron–ion interaction, namely ≈ 0.1–0.5 eV, is appreciably less than is observed experimentally. The polarization of the $4d$ core electrons should also make its contribution to such a shift. However, taking into account the fact that the polarizability of these core levels is extremely small, it is difficult to come to a final conclusion about the adequacy of this additional shift for obtaining the experimental value of the plasma energy in indium.

Structural features associated with the excitation of these core levels are characterized by much lower intensity than predicted by the latest theoretical calculations.[11] A similar situation also arises for metallic cadmium.[2,11] It should be noted that the exact shape and intensity of the polarized resonance in the calculated spectrum is much more sensitive to the choice of the approximation for the polarizability of the ion cores than is the shift produced by this polarization. In fact, the correct position of the plasma resonance is well reproduced, as shown by Sturm *et al.*,[11] where a relatively accurate approximation was used for the polarizability of the $4d$ levels in indium, and also by Sturm,[10] where this approximation is rather crude. At the same time, both the shape and the amplitude of the polarization resonance in Ref. 10 and 11 are quite different.

Undoubtedly the calculation by Sturm *et al.*[11] agrees much better with experiment from the point of view of describing the polarization resonance. The relatively low intensity of the polarization resonance in indium, its threshold character and the increase in amplitude of this resonance on passing from indium to cadmium are correctly reproduced by Sturm *et al.*[11] The disagreement with experiment in the amplitude and exact shape of the polarization resonance could probably be appreciably reduced by giving up a number of approximations made by Sturm *et al.*,[11] the most important of which can be ascribed to the neglect of spin–orbit coupling and also the finite width of the $4d$ levels. Since the desired goal is to reduce the amplitude of the polarization resonance in the computed spectrum, the overall contribution from the polarizability of these levels must be reduced. So far it is not known whether a correct representation of the position of the plasma peak will be given under these conditions.

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