

Surface-Photoelectric-Yield Spectrum of Indium below the Plasmon Energy

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(Received 15 October 1980)

The surface photoelectric yield of indium has been obtained by measuring *in situ* the total yield and the reflectivity for *s* and *p* polarizations on ultrasmooth evaporated films with preferential (111) orientation. With use of a theoretical calculation of Feibelman, it is shown that it is possible to extract the surface potential from the data in the energy range $0.6 < \omega/\omega_p < 1$. It deviates strongly from the corresponding Lang-Kohn result.

PACS numbers: 78.20.Dj, 78.20.Jq

This Letter reports on the directly optically excited surface photoelectric yield of indium. In the independent-particle model, if we consider the interaction Hamiltonian during the photoemission process, the surface photoeffect originates from (i) the strong component of the near-surface one-electron potential gradient along the surface normal and (ii) the important spatial variation, on an atomic scale, of the near-surface component of the screened vector potential normal to the surface.

In consequence, in the case of *atomically smooth surface*, this effect is only excited by *p*-polarized light. Then one can expect information on this effect from polarization study of the total yield and especially from deviations of the ratio $Y_p(\theta_i, \omega)/Y_s(\theta_i, \omega)$ from the result expected in an isotropic volume model:

$$\begin{aligned} & |\vec{A}_p^{in}(\theta_i, \omega)|^2 / |\vec{A}_s^{in}(\theta_i, \omega)|^2 \\ &= [1 - R_p(\theta_i, \omega)] / [1 - R_s(\theta_i, \omega)], \end{aligned}$$

where R_p , \vec{A}_p^{in} and R_s , \vec{A}_s^{in} are the reflectivities and vector potentials inside the film in *p*- and *s*-polarized light, respectively, and Y_p and Y_s are the total yields measured with *p*- and *s*-polarized light.

A number of experiments have been done to study the variation of this so-called "vector ratio" with the angle of light incidence θ_i and some of these results suggest direct optical excitation of the effect on polyvalent metals Mg and Al near threshold.^{1,2} Polarization studies at a fixed angle of incidence, but with variable photon energy, were performed by Monin and Boutry³ on alkali metals and their data contain the surface yield spectra for these metals; however, they have not tried to obtain information from their results on the surface photoelectric effect. More recently, Petersen and Hagström⁴ reported the experimental surface photoyield spectrum of aluminum by

exploiting the polarization properties of synchrotron radiation. But their data below the volume-plasma frequency are dominated by roughness-induced yields via decay of surface plasmons, both in *s* and *p* polarization, and thus any determination of the directly optically excited photoeffect would require a precise knowledge of the polarization dependence of the roughness-induced yields.

In this Letter, I report experiments of reflectivity and photoyields on indium, done with *s* and *p* polarization, on supersmooth films at 77°K. These results allow one to obtain the surface photoyield spectrum, after properly taking into account the variation with polarization of residual roughness-induced yields. The results are then compared with the theoretical calculations of Feibelman⁵ and the excellent agreement obtained below the volume-plasmon frequency allows us to deduce the shape of a model one-electron surface potential of indium.

The experiments were performed at the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, the Orsay Synchrotron Radiation Center, at the exit slit of a normal-incidence monochromator with a degree of polarization of 80%. The samples were opaque films. They were prepared by *in situ* evaporation onto smooth quartz substrates maintained at liquid-nitrogen temperature in order to obtain nonscattering films. During the evaporation, the pressure remained lower than 5×10^{-9} Torr and then dropped to its initial value (5×10^{-11} Torr) within 1 or 2 min. To avoid anomalous absorption due to structural disorder in the films, the samples were annealed (200°K) and then recooled (77°K) prior to measurements. This treatment produces polycrystalline samples whose grains are oriented with the (111) axis normal to the substrate.⁶ The surface of these samples is almost atomically flat, as can be inferred from a fit of the surface-

plasmon dip in the normal-incidence reflectivity curves to theory. A good fit was obtained with the theory of Elson and Ritchie for surface-plasmon excitation⁷ modified to take into account ϵ_2 ,⁸ by using a Gaussian autocorrelation function for the surface with the following values for the autocorrelation length and rms variation of the surface height about its mean value σ : $a \approx 300 \text{ \AA}$, $\sigma = 5-7 \text{ \AA}$.

Spectra of photoyields normalized to the photon flux of the monochromator and reflectivities were obtained on the same sample. Successive measurements with light polarized parallel (p) and perpendicular (s)¹⁰ to the plane of incidence were achieved by rotating the complete experimental system around the light-beam axis. Normalization to the photon flux was done by using a sodium-salicylate-coated photomultiplier and a National Bureau of Standards windowless Al_2O_3 -coated photodiode.

Figure 1 shows a set of photoyields versus photon energy below the volume plasmon frequency. The six upper curves correspond to p -polarized light (angles of incidence 15° , 20° , 30° , 35° , 40° , and 45°) and the lower curve to s -polarized light (angle of incidence 45°). I have represented only one curve for this polarization, as all of them have the same shape. The small roughness of the films allows a clear separation between the following: (i) The directly optically excited sur-

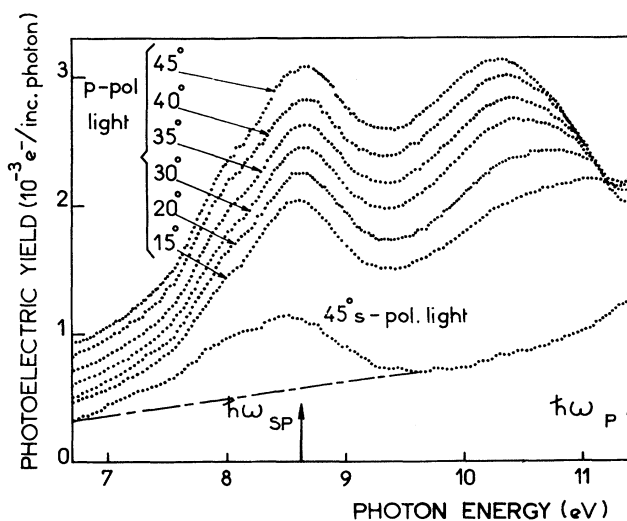


FIG. 1. Total photoelectric yield of In vs photon energy for various angles of light incidence. The dash-dotted curve corresponds to a smooth interpolation between the high- and low-energy side of the surface-plasmon-induced peak.

face photoelectric effect, not excited in s -polarized light, which gives a broad maximum between the surface and the volume plasmon energy. This maximum is more important as the angle of incidence varies from 15° to 45° (as expected, due to the increase in the normal component of the vector potential). (ii) The surface-plasmon-induced photoelectric yield which peaks at 8.55 eV in both s and p polarization, close to the theoretical surface plasmon value 8.65 eV ($\epsilon_1 = -1$).

One can, from this figure, make an estimate of the relative intensity of the roughness-induced yields measured at a given angle in p -polarized and s -polarized light, simply by smoothly interpolating between the low- and high-energy side of the surface-plasmon-induced peak as indicated in the figure (the surface photoelectric yield, peaking at higher energy, is not expected to exhibit structure there). The experimental values thus obtained for this ratio at different angles of incidence are very close to the curve representing the variation of the absorptance ratio $(1 - R_p)/(1 - R_s)$ with angle of light incidence.

The "isotropic-volume-model" vector ratio was then used to describe the polarization dependence of the surface-plasmon-induced yield. This ratio was obtained directly, by measuring the reflectivities $R_p(\theta_i)$ and $R_s(\theta_i)$, and via a determination of the optical constants of the films (normal-incidence reflectivity measurements) plus a separate measurement of the rate of polarization of the light. One can then extract the surface yield spectra

$$Y_{\text{surf}}(\theta_i) = Y_p(\theta_i) - Y_s(\theta_i) [1 - R_p(\theta_i)] / [1 - R_s(\theta_i)];$$

the results¹¹ are shown in Fig. 2(a) for the angles 15° , 30° , 45° , and 70° . As expected in the vicinity of the volume-plasmon energy $h\omega_p$, the surface yield goes to zero because of shielding of the normal component of the vector potential. One can already note that for all angles the maximum is shifted from the surface-plasmon frequency, in disagreement with Endriz's¹² theory. The surface yield spectrum divided by the quantity $|A_z(0^-)|^2 / |\bar{A}_{\text{inc}}|^2 \cos^2 \theta_i$ is shown in Fig. 2(b) for the same angles. In this last expression $A_z(0^-)$ is the normal component of the vector potential in the bulk calculated via standard Fresnel optics with previously determined optical constants of the films and \bar{A}_{inc} the incoming-light vector potential. This quantity for an atomically flat film, should result in a characteristic curve

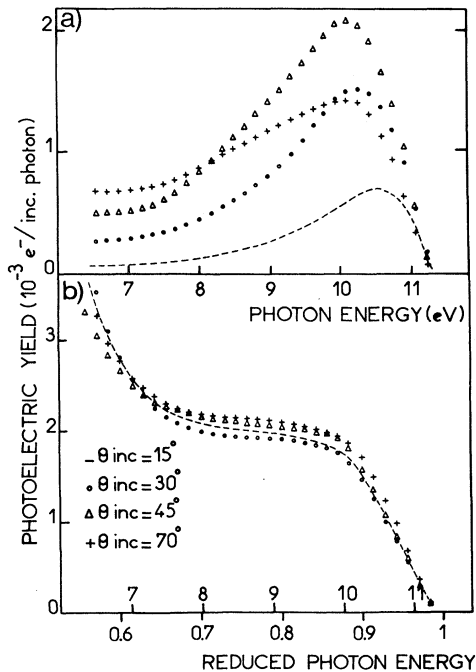


FIG. 2. (a) In surface photoelectric yield for different angles of light incidence. (b) In normalized surface photoelectric yield. The curves in (a) have been divided by the density of absorbed energy at $z=0$ corresponding to the normal component of the electric field inside the metal.

independent of angle of incidence,¹² so that at a fixed photon energy, the dispersion of the points gives an estimate of the accuracy of the results.

The main feature of this characteristic yield is a typical knee appearing near 10 eV. Among the different theoretical models applied to this problem (Mahan,¹³ Endriz,¹² Feibelman,⁵ Kliewer¹⁴), Feibelman's self-consistent calculation⁵ is the only one able to reproduce this feature (see, for example, the Fig. 2 of Ref. 5). It is beyond the scope of the present work to discuss these various calculations in detail. However, I should point out that the weakest point of Mahan's theory is the fact that he neglects the "refraction effects" while the results of Endriz and of Kliewer are typical of a step potential (through the result used for the electromagnetic response at the surface in Endriz's model).

I now proceed further into a comparison with Feibelman's calculations (Fig. 3). The experimental curve is the mean value of the characteristic yield defined in the previous paragraph. Feibelman's calculated curves are represented for two kinds of surface potential barriers:

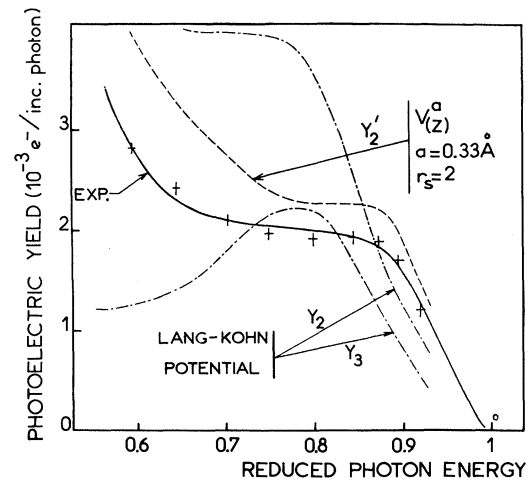


FIG. 3. Normalized surface photoyield of indium vs photon energy (full curve). The other curves correspond to Feibelman's calculations using Lang-Kohn potential (dash-dotted: Y_2 , $r_s = 2$; Y_3 , $r_s = 3$) and a parametrized potential (dashed). The crosses are interpolated points in order to fit the r_s value of indium [$Y_2' (0.6Y_2 + 0.4Y_3) / Y_2$].

(i) Lang-Kohn potentials for $r_s = 2$ and 3; (ii) a model potential $V_{r_s}^a(z)$ depending upon a parameter a , for $r_s = 2$ and $a = 0.33 \text{ \AA}$. The significance of a is that, when it decreases, the electron density profile at the surface becomes less and less diffuse.

Note that these calculations predict a sharpening of the electron density profile to decrease the photoyield magnitude and to shift the knee position towards the volume plasmon frequency, and that the photoyield magnitude also should decrease with increasing r_s . For indium, $r_s = 2.4$ and the agreement is better in shape with the parametrized curve ($r_s = 2$, $a = 0.33 \text{ \AA}$) than with the corresponding "Lang-Kohn" curve. Furthermore, if one interpolates linearly between the "Lang-Kohn" $r_s = 2$ and $r_s = 3$ curves in order to obtain an $r_s = 2.4$ curve and apply this interpolation function to the parametrized curve with $r_s = 2$ and $a = 0.33 \text{ \AA}$, one obtains the crosses, which are in remarkably good agreement with the experiment. Then a model one-electron potential for indium (111) should be taken considerably less diffuse than Lang-Kohn potential. This was also the theoretical prediction of Perdew and Monnier¹⁵ for the most densely packed face of fcc polyvalent metals Al and Pb (especially Pb).

Finally, I would mention that prior experimental data taken on smooth aluminum films [of preferential (111) orientation] lead to a model poten-

tial closer to the Lang-Kohn result. The data of Levinson and Plummer¹⁶ on normal photoemission from the Al(100) Fermi level are also correctly fitted with use of this potential. Thus a steeper potential is indicated for In than for Al and this result can explain the different shape of the surface-plasmon dispersion curves of Al and In obtained by Krane and Raether.¹⁷

I would like to thank Y. Pétrouff for suggesting the experiment, stimulating discussions, and critical reading of the manuscript and Professor H. Raether for pointing out to us his work on surface-plasmon dispersion.¹⁷ I am very indebted to A. Quémerais for experimental assistance and to the technical staff of Laboratoire pour l'Utilisation du Rayonnement Electromagnétique and members of the Laboratoire de l'Accélérateur Linéaire for providing the synchrotron beam facilities.

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¹⁰In the actual experiment, the degree of polarization of the light is 80%. However, for the sake of simplicity, I have kept the expressions *s*-polarized, *p*-polarized, R_s , R_p , Thus, *p* polarized refers to the situation where the major axis of the polarization ellipse is in the plane of incidence of light on the sample and *s* polarized to the case where the major axis is perpendicular to this plane.

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Electron-Spin-Resonance and Lattice-Parameter Study of Cerium Cubic Laves-Phase Compounds: Evidence for Intermediate-Valence State

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(Received 2 May 1980)

A lattice-constant study of the cubic $C15$ $Ce(Ir_xOs_{1-x})_2$ and $Ce(Pt_xIr_{1-x})_2$ mixtures at room temperature reveals anomalous lattice constant versus x behavior. Also the electron-spin-resonance thermal broadening and g shift of Nd^{3+} in these compounds are anomalous but could be correlated with the lattice parameters. This is taken as evidence for intermediate-valence state in some of the mixtures.

PACS numbers: 76.30.Hc, 61.55.Hg

Cerium and many of its intermetallic compounds are known to exhibit nonintegral valence.¹⁻³ The valence or the $4f$ occupation may change either continuously or discontinuously by varying the composition of the materials,^{1,4,5} external pres-

sure,¹ or temperature.^{1,6} Associated with valence change there are usually large changes in the lattice parameter and magnetic properties. Recently, concepts such as intermediate valence (IV) or interconfigurational fluctuations (ICF) have been