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Pressure dependence of the d-band to Fermi-level excitation threshold in silver

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The effect of pressure on the optical reflectivity edge of Ag at 3.8 eV has been measured up to 200 kbar. From the shift of the reflectivity edge the pressure dependence of the optical excitation threshold E_{dF} between the top of the $4d$ band and the Fermi level is determined. E_{dF} is nearly constant over a 13% volume reduction ($dE_{dF}/d\ln V = -0.3$ eV). The experimental result is compared to the linear muffin-tin orbital energy-band calculations of Perrot.

INTRODUCTION

The results of ground-state energy-band calculations of d-band metals at reduced volume depend critically on changes of d bandwidth and energetic position of the d-band complex with respect to sp-like states.[1,2] Calculations are usually checked against experimental bulk properties such as, e.g., the pressure-volume (PV) relation or the bulk modulus at normal volume. Spectroscopic information on the electronic eigenvalues of d states in d-band metals under pressure is scarce. Exceptions are the noble metals.

Prominent structure in the visible and near-ultraviolet optical absorption of the noble metals arises from interband transitions between the top E_d^t of the filled d-band region and empty sp-like states above the Fermi level E_F.[3] The onset of interband absorption results in sharp reflectivity edges at 2.1, 3.8, and 2.5 eV in Cu, Ag, and Au, respectively. Thus, the pressure dependence of the reflectivity edges in noble metals yield information on the pressure-induced change of the optical excitation E_{dF} between E_d^t and E_F.

Pressure effects on E_{dF} in noble metals have previously been investigated up to 11 kbar hydrostatic pressure[4] and in piezo-optical measurements.[5,6] The results demonstrate that E_{dF} increases slightly ($dE_{dF}/d\ln V \cong -1$ eV) in Cu and Au at reduced volume. Zallen[4] has reported a somewhat larger volume coefficient (-2.8 eV) for E_{dF} in Ag.

We have investigated the d-band—Fermi-level separation in Ag at pressures extending to 200 kbar. At this pressure Ag is compressed to 87% of its normal volume. Among the noble metals, silver was chosen partly because the recent linear muffin-tin orbital (LMTO) self-consistent ground-state calculations of Perrot[7] allow direct comparison with one-electron energy-band theory. E_{dF} is found to be almost independent of pressure, i.e., the volume coefficient is considerably lower compared to Zallen's result. This difference is explained by taking into account L-point $p \rightarrow s$ transitions ($L_2' \rightarrow L_1$), which at moderate pressures also contribute to the optical response of Ag near the 4-eV interband transition threshold.

EXPERIMENT

The optical reflectivity of Ag was measured by using a gasketed diamond anvil cell and a micro-optical system. Details of the apparatus have been presented elsewhere,[8] and diamond anvil techniques have recently been reviewed by Jayaraman.[9] The samples used were polycrystalline material. Reflection spectra were recorded for two different sample mountings. In the pressure range 0—60 kbar, annealed foils (20 μm thickness) were embedded in a 4:1 methanol-ethanol pressure medium. For measurements at higher pressures, the gasket hole was completely filled with the sample material and the reflectivity was measured at the sample-diamond interface. Pressures were determined from the ruby fluorescence shift using a pressure coefficient 0.365 Å/kbar.[9]

RESULTS AND DISCUSSION

Optical reflection spectra of Ag between 3.7 and 4.2 eV are displayed in Fig. 1. Figure 1(a) shows spectra mea-

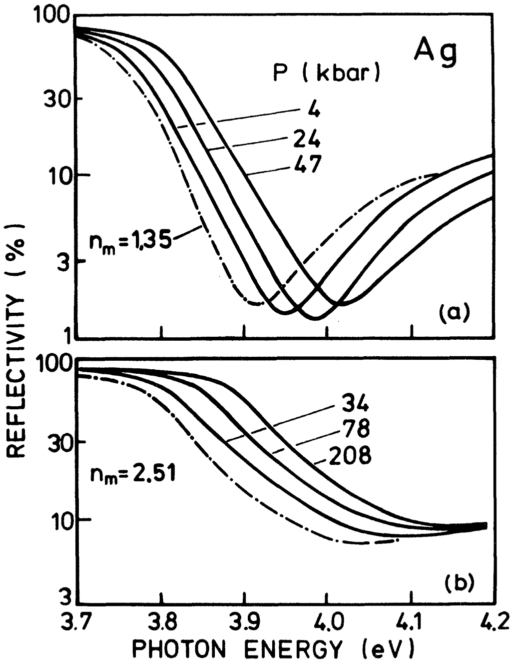

FIG. 1. High-pressure optical reflection spectra of Ag (solid lines) in the vicinity of the 4-eV interband absorption threshold. Spectra are measured (a) at the interface between sample and methanol-ethanol pressure medium, and (b) at the sample-diamond interface. Dashed-dotted lines represent normal-pressure reflection spectra calculated from the optical constants of Ref. 10.

sured under hydrostatic conditions at the interface between sample and methanol-ethanol pressure medium. The pressure-induced shift of the reflectivity edge is a combination of two effects: the change in the dielectric properties of the sample and the increase of the refractive index n_m of the liquid pressure medium. Figure 1(b) shows reflection spectra taken under quasihydrostatic conditions at the diamond-sample interface. Included in Fig. 1 are reflection spectra at normal pressure, calculated from the optical constants given by Winsemius *et al.*[10] for $n_m = 1.35$ and 2.51. The latter two values correspond to the refractive indices of the methanol-ethanol mixture ($P = 1$ bar) and diamond, respectively, at 3.8 eV.

The energetic position E_{edge} of the reflectivity edge as a function of volume is shown in Fig. 2. Pressures have been converted to volume using the PV data of Ref. 11. We define E_{edge} as follows: The onset of interband absorption in Ag results in a steep increase of the imaginary part $\epsilon_2(\omega)$ of the dielectronic function.[10,12–15] At normal pressure the intersection of the tangents to $\epsilon_2(\omega)$ below and above the threshold is taken as the edge position. This energy is 3.87 eV according to the results of Ref. 10, and coincides with the position of the reflectivity minimum for $n_m = 1$. For every experimental condition characterized by $n_m(P)$ we calculate normal-pressure reference spectra with the optical constants of Ref. 10. The pressure-induced shift of E_{edge} is then evaluated at the reflectivity level corresponding to $\hbar\omega = 3.87$ eV in the reference spectrum.

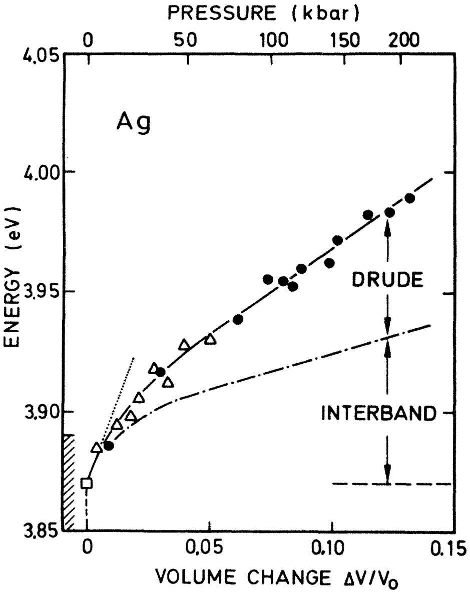

FIG. 2. Energetic position of the optical reflectivity edge of Ag versus volume. Triangles and circles correspond to hydrostatic and quasihydrostatic pressure conditions, respectively. The solid line is a guide to the eye. The dashed-dotted line represents the position of the reflectivity edge after the Drude contribution is subtracted from the experimental data. The open square marks the edge position at normal pressure (Ref. 10). The shaded region indicates the energy range of the normal-pressure edge position derived from other sources in the literature (e.g., Refs. 12–15). The dotted line corresponds to an extrapolation of Zallen's data (Ref. 4).

The refractive index of the methanol-ethanol mixture under pressure is obtained from the PV relation and the Clausius-Mossotti formula in the same manner as described by Welber *et al.*[16] The refractive index of diamond is assumed to be independent of pressure. A simple estimate based on the Phillips—Van Vechten empirical dielectric theory[17] and the bulk modulus of diamond yields $|\Delta n| < 0.05$ at 200 kbar hydrostatic pressure. The nonhydrostatic strain situation in the diamond window is not expected to induce changes considerably larger than the hydrostatic pressure effect.

It is evident from Fig. 2, that within the experimental scatter of about 5 meV, there is no difference between results obtained under hydrostatic and quasihydrostatic pressure conditions, respectively. Uniaxial effects on E_{edge} would be expected to be 1 order of magnitude smaller than the total shift observed in the present pressure range, because the yield strength of Ag is only a few percent of the maximum pressure.[11]

With $E_{\text{edge}} = 3.87$ eV as the normal-pressure reference energy, the shift of the reflectivity edge exhibits a considerable initial nonlinearity. The value of E_{edge} as defined above ranges from 3.85 to 3.89 eV (shaded range in Fig. 2) for other literature sources (see, e.g., Refs. 12—15). The spread of values is presumably due to samples of different types and the use of different techniques.[18] Thus, there is some arbitrariness in the backward extrapolation of Fig. 2. However, by choosing the extrapolation as shown, the initial slope of the E_{edge}-versus-$\Delta V/V_0$ curve roughly agrees with Zallen's result,[4] which was obtained by reflection and absorption measurements in the 10-kbar pressure range. In order to determine the pressure coefficient of the interband absorption threshold E_{dF} from the experimental data in Fig. 2, we have to consider in detail the effects contributing to the shift of the reflectivity edge.

Firstly, the dielectric constant $\epsilon(\omega)$ can be decomposed into a free-electron (Drude-like) contribution ϵ^f and an interband contribution ϵ^{ib} in the way originally demonstrated by Ehrenreich and Phillip.[15] The change of ϵ^f under pressure is mainly due to the increase in electron density. It is an elementary step to calculate this change and the corresponding effect on the position of the reflectivity edge, if ϵ^{ib} is kept constant. The dashed-dotted line in Fig. 2 represents the shift of the reflectivity edge after the free-electron effect is subtracted from the experimental data. It is only this remaining pressure effect which can be attributed to the change of the interband contribution ϵ^{ib}.

The second step is to consider the relation between interband absorption near 4 eV and the band structure of Ag. While in Cu and Au the $E_d^t \rightarrow E_F$ transitions are well separated in energy from other transitions, the onset of the *d*-band—Fermi-level absorption in Ag coincides with the $p \rightarrow s$ threshold near the L point $[L_2'(E_F) \rightarrow L_1]$. Details of the band structure of Ag near L are shown in Fig. 3. Experimental energy separations are collected from optical,[10] piezo-optical,[19,20] and photoemission studies.[21,22] The neck radius is taken from de Haas—van Alphen measurements.[23] The transitions between E_d^t and E_F arise from extended regions of the Brillouin zone near L and X.

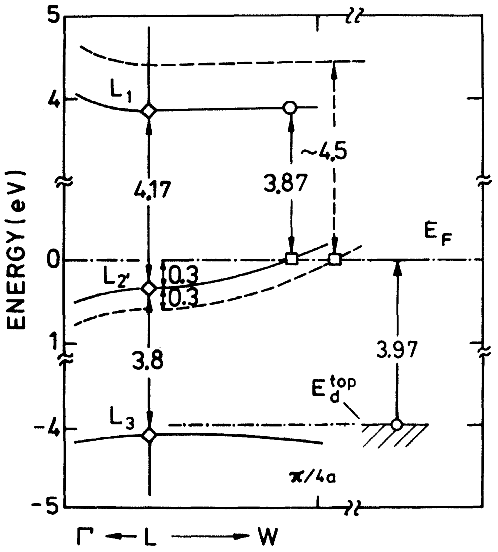

FIG. 3. Experimental band structure of Ag ($T=300$ K) near the L point at normal volume (solid lines). Open circles, diamonds, and squares represent results from optical, photoemission, and Fermi-surface studies, respectively. Dashed lines indicate the estimated change of the upper two bands with respect to E_F at a 10% volume reduction.

They commence at about 0.1-eV-higher energy compared to the p-s transitions near L.

The total experimental shift of E_{edge} is 1 order of magnitude smaller compared to typical pressure effects on the splitting of sp bands. In fact, the change of the $L_2'(E_f)\rightarrow L_1$ transition in Ag should be very similar to the corresponding transitions in Cu and Au listed in Table I. We adopt the value $dE_{p\rightarrow s}/d\ln V=-9$ eV for Ag. A 10% volume change would then increase the $E_{p\text{-}s}$ gap as indicated by the dashed lines in Fig. 3. The change of the neck radius is extrapolated from high-pressure de Haas–van Alphen measurements.[25] Obviously, the initial increase of E_{edge} must be attributed to the fast rise in the $p\rightarrow s$ transition threshold, which quickly moves out of the region of $E_d^t\rightarrow E_F$ transitions. The initial experimental volume coefficient is, however, smaller compared to typical values for sp gaps due to the overlap with $E_d^t\rightarrow E_F$ transitions, which only at pressures above 20 kbar predominantly determine the position of the edge. The linear volume coefficient of E_{edge} between 20 and 200 kbar (after correction for the Drude contribution; dash-dotted line in Fig. 2) is $dE_{\text{edge}}/d\ln V=(0.3\pm0.1)$ eV. This value is then identified with the volume coefficient $dE_{dF}/d\ln V$. Backward extrapolation of the linear portion of the "interband" line in Fig. 2 yields $E_{\text{edge}}=3.90$ eV at normal pressure. The difference to the value $E_{dF}=3.97$ eV, given in Fig. 3, is due to the definition of E_{edge}.

TABLE I. Experimental deformation potentials ($dE/d\ln V$) (in eV) of energy differences in noble metals. B_0 is the bulk modulus (in kbar). The present value for Ag is corrected for the Drude contribution (see text).

	L_1-L_2'	E_F-L_3	B_0
Cu	-9.3^a -9.6^b	-1.1^b	1330^e
Ag		-0.3^c	1060^f
Au	-9^d	-0.8^d	1660^e

[a] Reference 4.
[b] Reference 5.
[c] Present work.
[d] Reference 6.
[e] Reference 24.
[f] Reference 11.

Empirical band calculations of the optical properties of Ag by Lässer *et al.*[26] at normal volume yield about equal strength for the $d\rightarrow p$ and $p\rightarrow s$ transitions near 4 eV. The present experiment suggests, in accordance with temperature-dependent optical studies,[10,27,28] that the contribution of $p\rightarrow s$ transitions to the dielectric response of Ag at the interband transition threshold is significantly weaker than the $d\rightarrow p$ contribution. One argument is that the shape of the reflectivity edge is almost independent of pressure. In particular, if the $p\rightarrow s$ contribution was of comparable strength in the threshold region, one would expect that under pressure, the energy, at which $\epsilon_1=n_m$, would shift to a higher value compared to the onset of $E_d^t\rightarrow E_F$ transitions, i.e., the condition for observing a pronounced reflectivity minimum ($\epsilon_1=n_m$, $\epsilon_2\ll1$) would no longer be valid.

Finally, the present experimental result is compared to

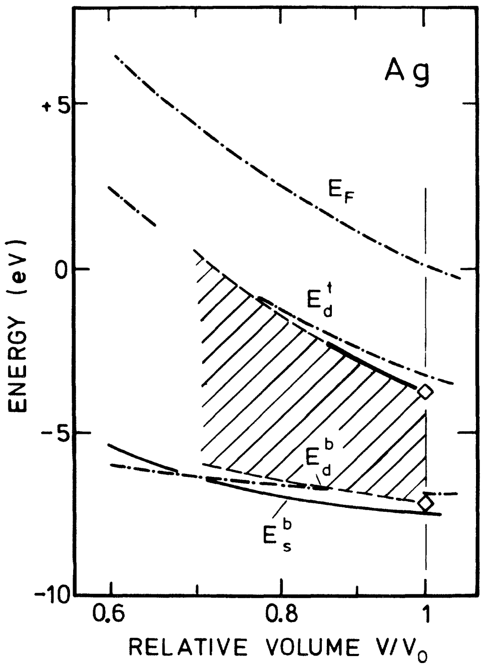

FIG. 4. Volume dependence of energy bands in Ag. The bottom of the 5s band E_s^b is described by an Ashcroft empty-core pseudopotential (Ref. 2). The dashed-dotted lines represent the calculated results (Ref. 7) for the bottom E_d^b and top E_d^t of the 4d band at X and for the Fermi level E_F, all three plotted relative to E_s^b. Open diamonds correspond to photoemission data (Ref. 22). The present experimental result and its extrapolation to smaller volume is represented by the upper solid and dashed lines. The lower dashed line is obtained by assuming an inverse five-thirds volume dependence for the width of the d band.

the recent ground-state LMTO band-structure calculation of Perrot,[7,29] which yields excellent agreement with experimental PV data over a 30% volume change. The calculated volume coefficients for the *d*-band—Fermi-level separation are $d[E_f - E(X_5)]/d\ln V = -1.9$ eV and $d[E_F - E(L_3)]/d\ln V = -2.5$ eV at the X and L points, respectively. Although these numbers are significantly larger than the experimental value -0.3 eV, the absolute magnitude must be considered as being small when compared to typical deformation potentials of *sp*-band splittings.

A schematic comparison between experimental data and theoretical results is given in Fig. 4, which shows the volume dependence of conduction-band energies in Ag. The figure is constructed as follows: The bottom of the conduction band E_s^b—described by an unscreened Ashcroft empty-core pseudopotential with parameters given by Pettifor[2]—is used as an energy reference. Perrot's calculated results for E_d^t, E_d^b (bottom of the d band), and E_F are plotted relative to E_s^b. The experimental *d*-band position at normal volume relative to E_F is taken from angle-resolved photoemission data.[22] The present result for the volume coefficient of E_{dF} yields E_d^t (experimental) as a function of volume, if we assume that $dE_{dF}/d\ln V \cong dE(X_5 \rightarrow E_F)/d\ln V$. From the experimental d bandwidth at $P = 1$ bar ($W_d = 3.5$ eV) and Heine's inverse five-thirds power law,[30] we estimate the volume dependence of E_d^b. On the energy scale shown in Fig. 4, the "experimental" and calculated *d*-band positions are in reasonable agreement. The present experimental data seem to indicate that at reduced volume the d band rises in energy slightly faster compared to the calculated *d*-band position.

This conclusion, however, is valid only if excitonic and local-field effects can be neglected. It has been suggested[31] that excitonic effects strongly influence the optical response of certain metals. These effects are sensitive to electron density, and may therefore also contribute to the pressure dependence of the dielectric response of Ag near the interband absorption threshold.

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