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THE EFFECT OF PRESSURE ON OPTICAL PROPERTIES OF THE NOBLE METALS *

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Abstract. Optical constants of the noble metals exhibit structure due to interband transitions in the visible and ultraviolet regions of the spectrum. The reflectivities of Cu, Ag and Au possess sharp cutoffs at photon energies of 2.1, 3.8 and 2.3 eV, respectively. Cooper, Ehrenreich and Philipp identify this structure with the onset of direct transitions from a flat, filled d-band to empty s-band states outside the Fermi surface. We have studied the pressure dependence of the d-band - Fermi level separation to 12 kilobars, at room temperature, by observing the shift with pressure of the reflectivity edge of Cu, Ag and Au, and of the transmission window of evaporated Ag films. In silver, this energy separation increases with pressure at a rate of $+(2.7 \pm 0.4) \times 10^{-6}$ eV/bar: in copper and gold the pressure coefficient is smaller in magnitude than 1×10^{-6} eV/bar. For silver, this pressure coefficient, along with a value obtained by Templeton for the pressure dependence of the neck radius, was used to deduce a pressure coefficient of $+(1.7 \pm 0.4) \times 10^{-6}$ eV/bar for the s-d splitting at the L-point. A pressure coefficient of $+(7 \pm 1.5) \times 10^{-6}$ eV/bar was estimated for the s-d energy gap at the X-point in copper by observing the motion under pressure of the reflectivity structure near 4.2 eV.

1. *Introduction*

The optical properties of the noble metals exhibit distinct structure in the visible and near ultraviolet. The dominant feature is a sharp drop-off in reflectivity at a photon energy much smaller than that expected from the free-electron plasma frequency. This behavior is understood, within the framework of one-electron energy band theory, in terms of interband transitions which begin to contribute to ϵ_2, the imaginary (absorptive) part of the dielectric constant, at these frequencies. In two recent publications, EHRENREICH and PHILIPP (1962) and COOPER, EHRENREICH and PHILIPP (1965) (henceforth referred to as EP and CEP, respectively), have accounted for this structure in Cu, Ag, and Au by means of the joint density of states for direct interband transitions obtained on the basis of electronic energy band structures calculated for Cu by SEGALL (1962) and by BURDICK (1963). CEP found that the interband contribution produces an edge in ϵ_2 which is responsible for the reflectivity edge in these metals. This interband absorp-

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tion edge corresponds to the onset of direct transitions from a flat filled d-band to empty conduction band states above the Fermi surface. In addition to this feature, which is specific to metals, there is structure in ϵ_2 at higher energies associated with Van Hove singularities at critical points in k-space (PHILLIPS, 1960).

In the present work, an experimental investigation of the effect of hydrostatic pressure on optical properties of the noble metals was undertaken in order to obtain information about the pressure dependence of the band structure of these materials. Optical-pressure experiments have been useful in studying the band structure of semiconductors (PAUL, 1961; ZALLEN and PAUL, 1964), but no such work on metals has come to the attention of the author. The current investigation yielded information about the pressure dependence of the Fermi-level - d-band energy separation in Cu, Ag, and Au. It was found that this quantity, denoted henceforth by E_{Fd}, is much more sensitive to pressure for Ag than for Cu and Au. Information was also obtained about the pressure dependence of the s-d splitting at the L-point in the Brillouin zone for Ag and at the X-point in the zone for Cu.

2. *Experimental techniques*

Since a detailed description of the apparatus used in these experiments has been presented elsewhere (ZALLEN and PAUL, 1964), only a brief discussion is needed here. For the reflectivity measurements, four samples were arranged in a periscope-like configuration immersed in isopentane inside a high pressure vessel equipped with sapphire windows. Light transmitted through the bomb experienced four 45° reflections from surfaces of the metal under investigation. The maximum pressure available was 12 kilobars. All measurements were made at room temperature. The samples used were polycrystalline slabs polished and, if necessary, etched to show the reported reflectivity structure.

In the case of silver, measurements also were made on the transmission of evaporated films deposited on quartz and sapphire substrates, and on unbacked films dissolved off rock salt substrates. The evaporations were performed at high deposition rates onto unheated substrates so that the resulting films were polycrystalline or amorphous.

3. *Results and discussion*

3.1 Ag reflectivity

The optical properties of Ag in the vicinity of 3.8 eV are shown in fig. 1 (TAFT and PHILIPP, 1961). Silver is remarkable for the sharpness of the structure in this region. The measurement of reflectivity under pressure discussed in this section determined the rate of shift of the steep portion of the reflectivity curve, indicated in fig. 1 by the section bordering the shaded area at the upper left.

Experimental results are shown in fig. 2 which shows the measured curves

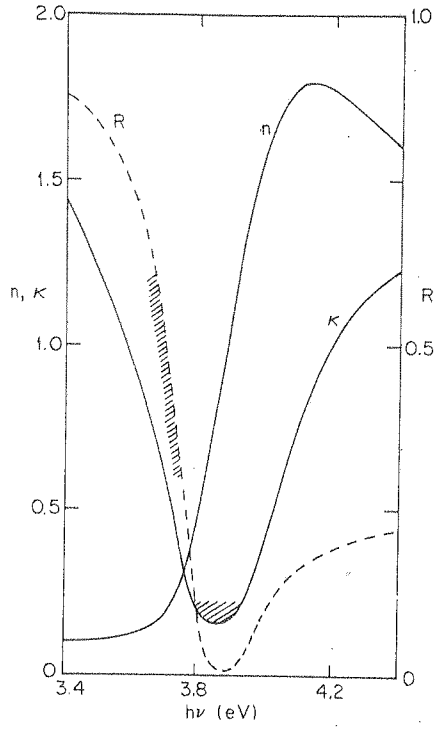

Fig. 1. The reflectivity R, refractive index n, and extinction coefficient κ of silver near the reflectivity edge (after TAFT and PHILIPP, 1961).

for silver in air, in isopentane at low pressure, and in isopentane at high pressure. The relative displacements of the three curves reflect a combination of two effects: the effect of pressure on the optical constants of the silver, and the effect of the (pressure-dependent) refractive index of the pressure fluid, n_1. That the latter, which must be corrected for, influences the observed position of the reflectivity edge may be seen by considering fig. 1. Since κ is small when the reflectivity passes through its minimum, the position of that minimum occurs when n passes through the value of the refractive index of the surrounding medium (unity in the case of fig. 1). Thus an increase in the index of the medium shifts the reflectivity curve to higher energies. (For Cu and Au, $\kappa > n$ near the edge, which is thus insensitive to n_1.)

The correction for the pressure dependence of n_1 was carried out in the following way. The compressibility data of BRIDGMAN (1931) was used to obtain the density of isopentane at the pressures shown in fig. 2. $n_1(P)$ was then computed from $n_1(0)$ by means of the Clausius-Mosotti relation. Assuming that the displacement between the curves for silver in air and in isopentane at low pressure is due entirely to the difference in n_1, and that this effect is linear in n_1, the shift due to the pressure dependence of n_1 between the low and high pressure curves of fig. 2 is then determined.

The result is indicated by the dashed curve in fig. 2, which represents the low pressure curve shifted by an amount appropriate to the change in n_1

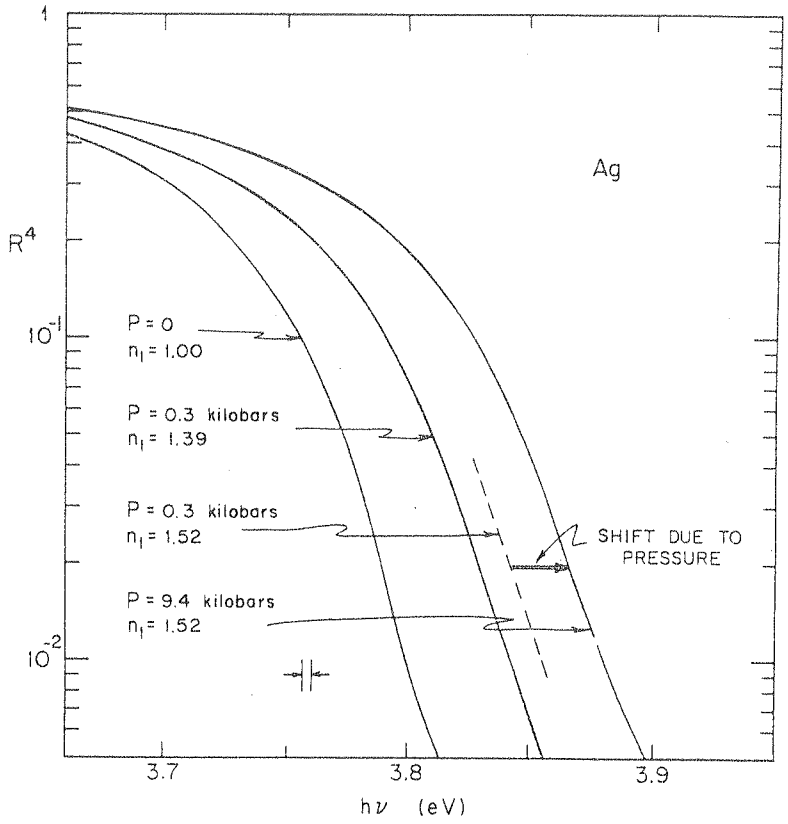

Fig. 2. Experimental results for the pressure dependence of the silver reflectivity edge. The dashed line represents the result of correcting the central curve to the high pressure value of n_1, the refractive index of the pressure fluid.

between low and high pressure. The displacement due to pressure of the structure in the optical constants of silver is then the shift between the corrected low pressure curve and the measured high pressure curve. The pressure coefficient thus obtained is $+2.7 \times 10^{-6}$ eV/bar.

3.2. Ag transmission.

The deep minima in κ and R shown in fig. 1 give rise to the well-known transmission "window" of silver in the ultraviolet. This circumstance provided an opportunity to obtain a second measurement of dE_{Fd}/dP by observing the effect of pressure on the position of the transmission band of evaporated Ag films. Films were prepared of sufficient thickness to ensure that the transmission curve was determined predominantly by the attenuation within the film rather than the reflection at the surfaces (i.e., by the minimum in κ rather than the minimum in R). Fig. 3 displays the shape of the transmission curve of a free silver film at low and at high pressure. The peak transmission is about 11%, implying a thickness of about one-third of a micron according to the optical constants of fig. 1. The shaded trough at

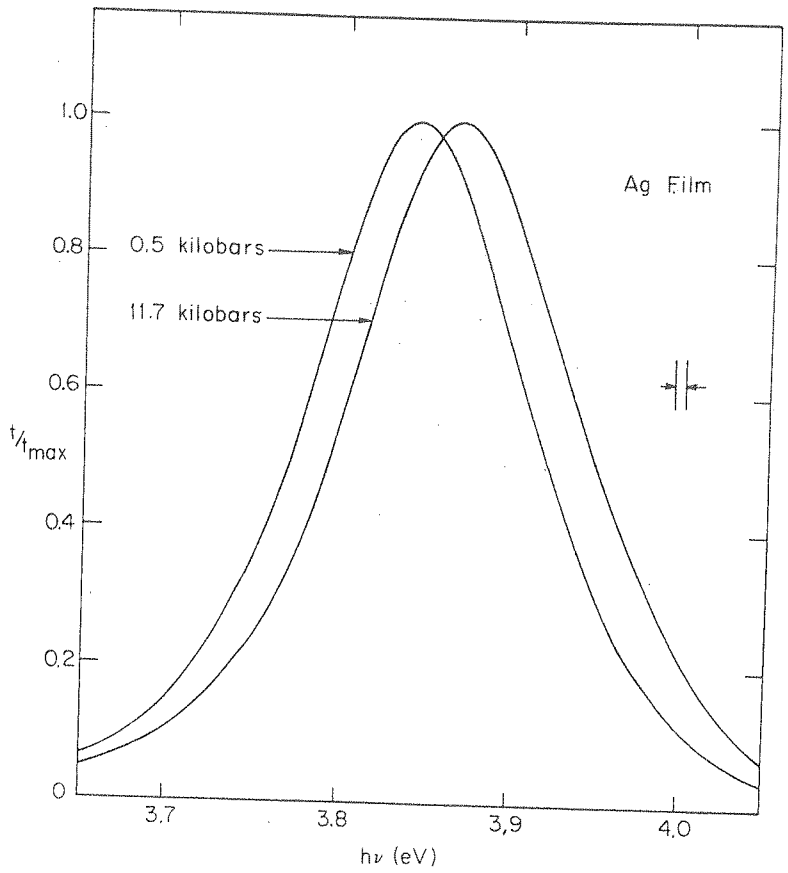

Fig. 3. The effect of pressure on the transmission of an unsupported silver film.

the bottom of the κ curve in fig. 1 corresponds to the part of the transmission curve for which $t/t_0 > 0.5$. R is small in this region and $(1-R)^2$ slowly varying in comparison with $\exp(-2\omega\kappa/c)$, so that the position of the transmission peak closely corresponds to the position of the extinction coefficient minimum. Moreover, since the reflectivity scarcely affects the shape of the transmission curve, the measurement is insensitive to the refractive index of the pressure fluid. No correction for $n_1(P)$ is needed as was necessary in the case of the reflectivity measurement of the preceding section.

Besides measurements on unsupported silver films, measurements were also made on silver films adhering to quartz and sapphire substrates. The motion of the transmission peak under pressure was quite different for the three cases, as is apparent from fig. 4a. The observed pressure coefficient increases in the order Ag on Al_2O_3, Ag, Ag on SiO_2, and in the last case there is a definite hysteresis and offset of the peak position after a pressure cycle. The explanation for this behavior lies in the unequal compressibility of substrate and film for the backed films, which causes a biaxial component of stress in the film, in addition to the isotropic stress, when hydrostatic

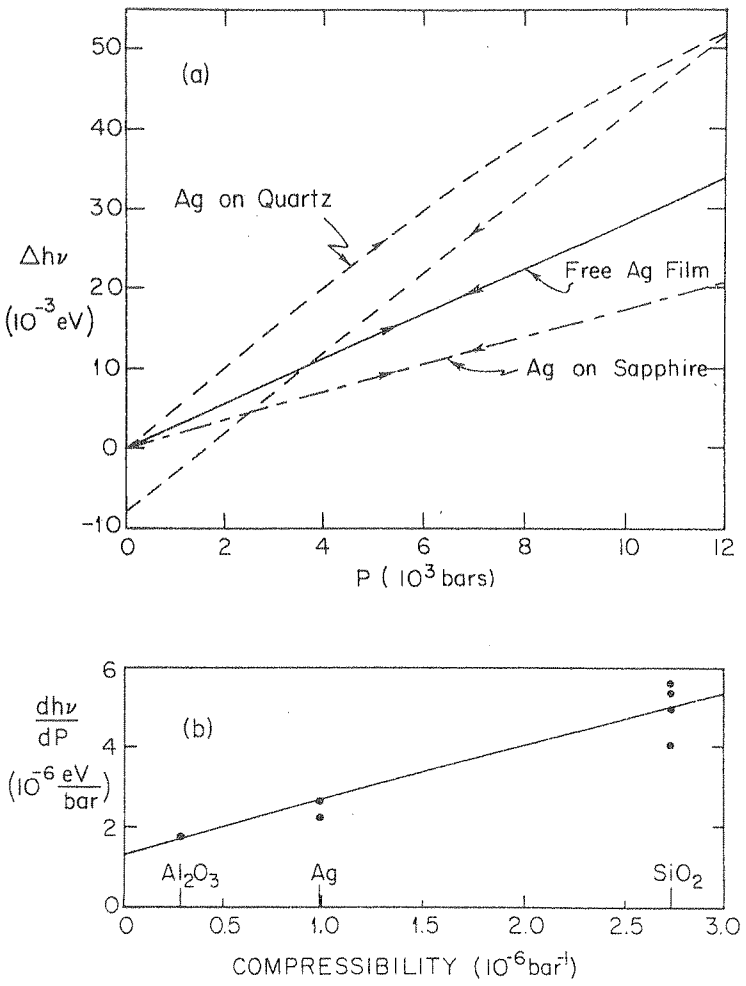

Fig. 4. (a) Displacement with pressure of the position of the transmission peak of an unsupported silver film and of silver films on quartz and sapphire substrates. (b) Pressure coefficient of the peak as a function of substrate compressibility.

pressure is applied to the system. With sapphire, less compressible than silver, biaxial tension is produced in the film. With easily compressible quartz, biaxial compression is produced. In the latter case, the difference in compressibility is great enough to cause the biaxial stress component to exceed the elastic limit within the accessible pressure range, which accounts for the hysteresis and offset exhibited by the dashed curve in fig. 4a.

In fig. 4b we have plotted the slopes of the curves of fig. 4a versus compressibility of the substrate. (For the unbacked film, the appropriate substrate compressibility is that of silver itself.) The intercept of the fitted straight line with the silver compressibility value yields a hydrostatic pressure coefficient for the transmission window of $+2.7 \times 10^{-6}$ eV/bar, in good

agreement with the value obtained for the reflectivity edge. (Since both determinations possess an uncertainty of the order of 15 or 20%, the exact agreement, although satisfying, is not of great significance.) Thus, for silver, the pressure coefficient of the Fermi level - d-band energy gap is given by

$$\text{(Ag)} \qquad \frac{dE_{Fd}}{dP} = +(2.7 \pm 0.4) \times 10^{-6} \frac{\text{eV}}{\text{bar}} . \tag{1}$$

A brief calculation was performed in an attempt to account quantitatively for the slope of the line in fig. 4b. The dilatation under pressure of a film constrained by a substrate can be shown to differ from that of a free film by a factor η given by

$$\eta = 1 + \frac{2}{9}\left(\frac{K_S - K}{s_{11} + s_{12}}\right), \tag{2}$$

where K_S and K are the substrate and film compressibilities, and s_{11}, s_{12} are compliance constants of the film. If dilatation alone is solely responsible for dE_{Fd}/dP, then this quantity for a backed film will equal the value for the free film multiplied by η, which is linear in K_S. To estimate η we assume that the polycrystalline film is elastically isotropic so that s_{11} and s_{12} may be computed from the single crystal compliance constants by means of averaging procedures described by HUNTINGTON (1958). The result obtained for the slope of dE_{Fd}/dP versus K_S is about three-fifths of the observed value. It is difficult to conclude whether the difference is due to experimental error or the crudeness of the computation, or whether it is a real effect. In the latter case, it would represent an explicit contribution to the energy shift of the biaxial distortion.

3.3. Cu and Au

The reflectivity edges in Cu (2.1 eV) and Au (2.3 eV) were measured to 10 kilobars. For both edges the shift was unobservable, the upper limit on $|dE/dP|$ being less than 1×10^{-6} eV/bar. Thus E_{Fd} is at least three times more sensitive to pressure for Ag than for Cu and Au, adding another distinction to the position of Ag among the noble metals.

In the range 4-5 eV, the noble metals exhibit a weak upturn in reflectivity and a peak in ϵ_2 ascribed by CEP to a Van Hove singularity associated with $X_5 \rightarrow X_4$, transitions. This structure is clearest in Cu, taking the form of a minimum or kink in R near 4.2 eV. The motion of this structure with pressure was measured and determined to be

$$\text{(Cu)} \qquad \frac{dE_X}{dP} = +(7 \pm 1.5) \times 10^{-6} \frac{\text{eV}}{\text{bar}} . \tag{3}$$

4. *The effect of pressure on the band structure*

Fig. 5a displays an energy band diagram representative of the noble metals, with $E(k)$ shown for several symmetry directions in the Brillouin zone. This diagram, which is a schematic version of the results of SEGALL's (1962) detailed band calculations for Cu, includes bands energetically close to the Fermi level: the s-band and the highest d-band. Two intersections with the Fermi surface, labelled by k_n and k_b, are shown. (In the vernacular, k_n and k_b are the "neck" and "belly" radii, respectively.)

The direct transitions proposed by EP and CEP to account for the primary edge in ϵ_2 take place between the d-band and empty s-band states above the Fermi level. The threshold energy for this process, represented by the vertical arrows labelled E_{Fd} in fig. 5a, is the energy gap whose pressure dependence was measured in our experiments on the optical structure in Ag at 3.8 eV, in Cu at 2.1 eV, and in Au at 2.3 eV. The energy separation labelled E_X in the figure corresponds to the critical-point transitions proposed by CEP for the 4.2 eV structure in Cu.

The upper d-band is depicted in fig. 5a as being perfectly flat, in which case the onset of vertical transitions would occur simultaneously over the entire Fermi surface. The actual width of the d-band is a few tenths of an eV, and the onset of direct transitions takes place near the L-points at the necks of the Fermi surface (left-hand E_{Fd} transition in fig. 5a). In fig. 5b, the band structure of Ag in the vicinity of an L-point is shown along a diagonal of one of the hexagonal faces of the Brillouin zone. E_{Fd} is known from the position of the reflectivity edge, and E_{FL} is the value calculated by CEP from the known effective mass and neck radius. This determines E_L, the s-d energy gap at the L-point. The pressure dependence of E_{Fd} was discussed in sections 3.1 and 3.2. Very recently, TEMPLETON (1965) has measured the effect of pressure on the neck radius in the noble metals by De Haas-Van Alphen experiments. For silver he finds that $(d \ln k_n)/dP$ is about $+1.9 \times 10^{-6}$ bar^{-1}. Assuming a constant mass, the pressure dependence of E_{FL} is given by

$$\frac{d \ln E_{FL}}{dP} = 2 \frac{d \ln k_n}{dP},$$

and dE_{FL}/dP is found to be $+1.0 \times 10^{-6}$ eV/bar. (The pressure dependence of the effective mass may easily be taken into account by means of the $k \cdot p$ expression given in equation (12) of CEP, and it is found to be unimportant.) The relative motion with pressure of Fermi level, d-band, and s-band is thus established. The pressure effect relative to the Fermi level is indicated by the dashed curves in fig. 5b, corresponding to a hypothetical pressure of 10^5 bars. The pressure coefficient of E_L is found to be:

$$\text{(Ag)} \qquad \frac{dE_L}{dP} = +(1.7 \pm 0.4) \times 10^{-6} \frac{\text{eV}}{\text{bar}}. \qquad (4)$$

The implicit temperature coefficient of E_{Fd} for Ag (i.e., the effect of the change in volume produced by thermal expansion), deduced from the observed pressure coefficient, is about -1.5×10^{-4} eV/°K. JOOS and KLOPFER

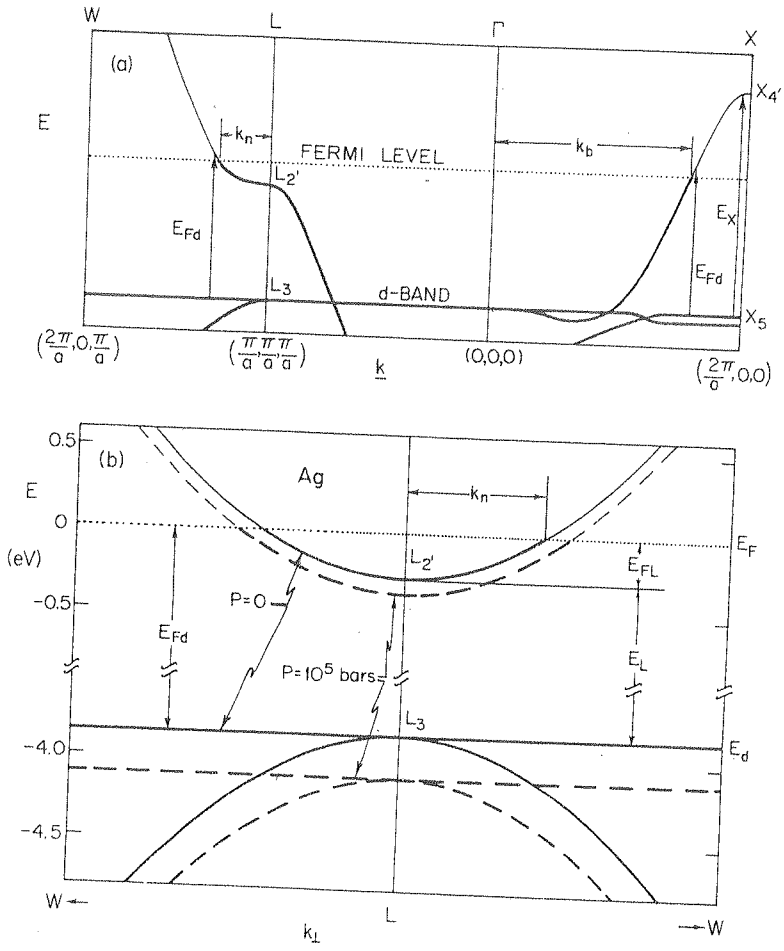

Fig. 5. (a) Typical noble metal band structure near the Fermi level. (b) Effect of pressure on the band structure of silver in the vicinity of an L-point.

(1954) found that the principal effect of temperature on the edge in ϵ_2 for Ag is a broadening explainable in terms of the Fermi function. However, the translational part of their reported temperature dependence is comparable to the above implicit temperature coefficient, implying that the explicit temperature dependence of E_{Fd} (due to electron-phonon interaction) is quite small.

5. *Summary*

The effect of pressure on the Fermi level - d-band energy separation was studied by means of reflectivity measurements for Cu, Ag and Au, and also by transmission measurements for the case of Ag. The pressure coefficient, dE_{Fd}/dP, was found to be $+(2.7 \pm 0.4) \times 10^{-6}$ eV/bar for Ag, and smaller in

magnitude than 1×10^{-6} eV/bar for Cu and Au. For Ag, the value of dE_{Fd}/dP and a reported value for the pressure dependence of the neck radius were used to deduce the pressure effect on the s-d splitting at the L-point: $dE_L/dP = +(1.7 \pm 0.4) \times 10^{-6}$ eV/bar. The pressure coefficient of the s-d splitting at the X-point in Cu was estimated to be $dE_X/dP = +(7 \pm 1.5) \times 10^{-6}$ eV/bar, from a reflectivity experiment.

Acknowledgements

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DISCUSSION

Remark by J. C. Phillips

The experimental results quoted here shed light on the nature of the reflectivity minimum at 4.2 eV in Cu. Ehrenreich and Philipp have assigned this minimum to $X_5 \rightarrow X_{4'}$ transitions (d → p transitions, in atomic nomenclature). In the preceding paper, Beaglehole suggested $L_{2'} \rightarrow L_1$ (p → s transitions). Also the threshold in Cu (vicinity of $L_3 \rightarrow L_{2'}$) has d → p character. Quite general arguments suggest that the pressure dependence of the two d → p transitions should be almost the same. On the other hand, there are two good reasons for believing that the pressure dependence of p → s transitions should be much larger. These are: (1) in semiconductors the "sensitive" transitions (PHILLIPS, 1962, Phys. Rev.) are of the p → s type, and (2) the band calculations of Segall and Burdick, which used slightly different methods in calculating the energy bands of Cu, agree well as regards the d and p bands, but give values for the s level L_1, which differ by 1 eV. Thus the s level L_1 is a sensitive one in Cu just as it is in Ge.

Experimentally, it is found that the 4.2 eV minimum in Cu is more than seven times more sensitive to pressure than the $L_3 \rightarrow L_{2'}$ edge. Thus it must be assigned to $L_{2'} \rightarrow L_1$ as suggested by Beaglehole.

Question by W. E. Spicer

Do you see any evidence that the optical peaks are made up of more than a single optical transition? The second Cu peak located at about 4.5 eV is of particular interest.

Answer by R. Zallen

If several transitions made comparable contributions to the same piece of optical structure, then this structure would be expected to broaden under pressure as the separate, unresolved components would in general shift with pressure at different rates. Fig. 3 shows little evidence of such an effect for the sharp structure in silver at 3.8 eV. Since the structure near 4 eV in Cu is much less distinct than that in Ag, it would have been more difficult to observe a broadening for that case; if it was present, it was not discernible in these measurements.

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