nearest-neighbor (nnn) perturbation model has revealed that there occur only insignificant changes in the nnn force constants. Thus, the inclusion of two more unknown parameters (nnn force-constant changes) in the present theory which would further complicate the situation does not seem to be worthwhile.

IV. CONCLUSIONS

The lattice specific heat of Mo with 5-at.%-Re alloy in the temperature range 1–14 °K can be well understood on the basis of a nearest-neighbor perturbation model, after considering changes in the central and noncentral force constants for the impurity–host-crystal interaction. Above 14 °K, the calculated specific heat does not show a T^3-dependent behavior. The contribution of force-constant changes to the specific heat is seen to be quite large, i.e., ~ 55% of the total enhanced specific heat. The specific heat is very sensitive to force-constant changes, especially to the noncentral part. The contribution of all the even-parity modes, i.e., A_{1g}, E_g, F_{1g}, and F_{2g}, are quite large and dominate over the contribution of the odd-parity F_{1u} modes in the low temperature of the specific-heat curve. However, at higher temperatures more resonance modes are excited and the contribution of F_{1u} symmetry modes dominates.

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Photoelectron Emission and the *d* Bands of Zinc and Cadmium

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The *d* bands of Zn and Cd have been unambiguously located by photoelectron spectroscopy using 40.81-eV radiation. In Zn a single peak due to the $3d_{3/2,5/2}$ band of half-width 1.1 eV is found 9.5 eV below Fermi level, while for Cd, the $4d_{3/2,5/2}$ doublet is resolved at 10.2 and 11.1 eV below the Fermi level. The relevance of these results for band-structure calculations and for the interpretation of related optical and characteristic energy-loss experiments is discussed.

INTRODUCTION

The suitability of the helium-II resonance line at 40.81 eV as a probe for band-structure studies has recently been recognized.[1] Evidence available to date[2,3] suggests that the energy distributions of photoelectron spectra generated by Al $K\alpha$ radiation and by 40.81-eV helium resonance radiation are closely similar, and it is reasonable to assume that the spectra so generated are representative of the density of occupied states of the irradiated materials.[4] Without use of predispersion, the resolu-

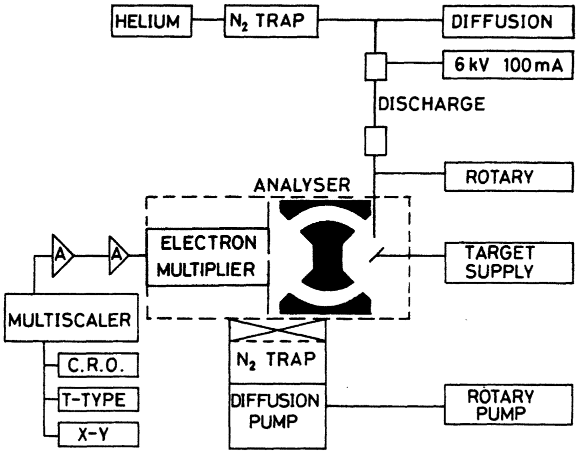

FIG. 1. Schematic diagram of the windowless spectrometer.

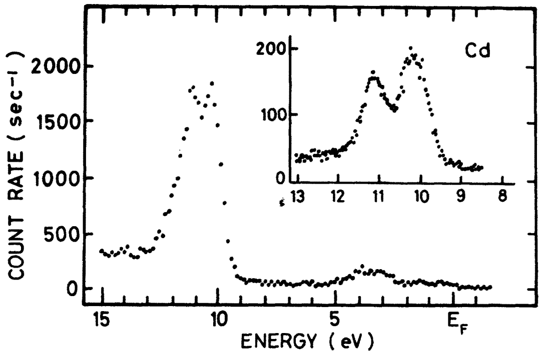

FIG. 3. Photoelectron energy distribution spectrum for cadmium using 40.81-eV photons. The $4d$ band is seen as a resolved peak centered at 10.7 eV (analyzer resolution 0.6 eV). At higher analyzer resolution (0.2 eV) the $4d_{3/2,5/2}$ peaks are more clearly resolved (insert) at 10.2 and 11.1 eV (±0.1 eV). The peak at 3.1 eV is a satellite due to 48.37-eV radiation.

tion obtainable from x-ray photoelectron spectrometers is limited by the natural linewidth of the Al $K\alpha_{1,2}$ doublet (~1 eV). In contrast, the resolution obtainable from uv photoelectron spectrometers is usually limited by the electron optics of the energy analyzer employed, since the inherent linewidth of resonance radiation is close to 0.1 meV. Most uv photoelectron spectra obtained in the past have been generated using photon sources with $\hbar\omega \lesssim 21.22$ eV. In this region, the energy distribution of photoelectrons is related to the energy distribution of the joint density of initial and final states[5]:

$$D(E,\hbar\omega) = (2\pi)^{-3}\sum_{if}\int |M_{if}|^2 \times \delta(E_f - E_i - \hbar\omega)\,\delta(E - E_i)\,d^3k\ ,$$

where the $|M_{if}|$ represents the dipole matrix elements between initial (E_i) and final (E_f) states. $D(E,\hbar\omega)$ is not presently available for the majority of materials and the interpretation of low-energy uv photoelectron spectra is further complicated by the presence in the energy distribution of electrons which have been inelastically scattered before emission. Although methods for dealing with such scattered electrons have been devised[6,7] it seems preferable to work with 40.81-eV radiation where such complications are largely absent.

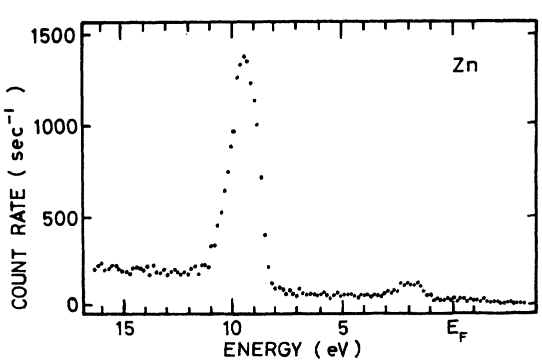

FIG. 2. Photoelectron energy distribution spectrum for zinc using 40.81-eV photons. The $3d$ band peak is located at 9.5±0.1 eV. The smaller peak at 1.9 eV is a satellite due to 48.37-eV radiation. Analyzer resolution was 0.6 eV.

EXPERIMENTAL ARRANGEMENT AND RESULTS

The spectrometer used in the present experiment, shown schematically in Fig. 1, employs resonance radiation produced by a dc-capillary discharge lamp. The radiation is introduced into the main vacuum envelope via a differentially pumped capillary where it is allowed to strike a freshly evaporated sample. The 90°-sector spherical electrostatic analyzer is operated at a fixed pass energy, the spectra being obtained by applying a staircase voltage between the sample and the entrance aperture of the analyzer. This voltage is synchronized with the channel advance mechanism of a multiscaler. The resolution of the system is directly related to the pass energy of the analyzer and has been measured as 50 meV at a pass energy of 2.5 eV. The relative intensity of 40.81-eV/21.21-eV radiation produced by the lamp is strongly dependent on helium pressure, being approximately 25% for pressures in the low 10^{-2}-torr region. The spectrometer is operated in the constant-energy mode[8] with the consequent advantage that the resolution is invariant with changing photoelectron kinetic energy, while the absolute transmission efficiency of the instrument has been determined experimentally. The method of calibra-

TABLE I. Valence-band data for zinc. Summary of calculations and observations of electron energy-band structure for zinc. In particular, structure in the region of 10 eV below the Fermi level is tabulated, and the third column indicates the brief conclusion or theoretical method for the explanation of this structure as proposed in the indicated reference papers.

Type of calculation/ experiment	Position of structure relative to Fermi level (eV)	Remarks	Ref.
Modified orthogonalized-plane wave	−8	Early pseudopotential theory result	11
Augmented-plane wave	−17	Preliminary results	12
Empirical pseudopotential	−11	Place d bands closely below bottom of s–p bands; spin-orbit coupling included	13
APW	−20	Full Slater exchange: no dynamical corrections	14
APW	−6.8	$\frac{2}{3}$ Slater exchange: no dynamical corrections; width ~ 2 eV	14
KKR	−8.5	$\frac{5}{6}$ Slater exchange	10
Plasma radiation	−8.6	Identified as either volume plasmon energy or d structure	21
Optical reflectance	−10.1	Interpreted as due to plasma resonance	20
Soft x-ray	−10.6	$3d_{3/2,5/2}$ levels unresolved	17
Soft x-ray spectroscopy	−8.4	$3d_{3/2,5/2}$ levels unresolved	15
X-ray photoelectron spectroscopy (XPS)	−8.9	$3d_{3/2,5/2}$ levels unresolved	18
Plasma resonance	−9.46	Interpreted as due to volume plasmons but expected dispersion not found	16
Characteristic energy loss	−8.6	Structure located at −8.6 and 17.0 eV: relatively poor resolution	22
UPS (21.22 eV)	−9.5	d-band structure	19
Various	−8.1 ± 0.6	Survey up to 1967	23
UPS (40.81 eV)	−9.5 ± 0.1	$3d_{3/2,5/2}$ levels unresolved	Present work

tion and further details of the design and construction of the He lamp and spectrometer will be given in future publications.

Photoelectron spectra from freshly evaporated thin films of Zn and Cd taken at ambient temperatures are shown in Figs. 2 and 3. The spectrometer in both cases was operated at a resolution of 0.2 eV in order to increase the count rate and so minimize the chances of surface contamination. System pressure was maintained in the 10^{-8}-torr range, and all measurements were completed within 1 min following *in situ* evaporation onto the Al substrate. The detailed structure of the thin films used was not investigated. The absence of any structure representative of zinc oxide in Fig. 2 may be seen by comparing the present result with the x-ray photoelectron spectroscopy (XPS) results for ZnO published by Langer and Veseley.[9] Both the Zn and Cd spectra reported here also clearly contain little contribution from inelastically scattered electrons. The insert in Fig. 3 also shows two resolved peaks for Cd at 10.2 and 11.1 eV relative to the Fermi level E_F. The deconvoluted areal ratio of these peaks is approximately 4 : 6, in accordance with the electron population of the $4d_{3/2,\ 5/2}$ states.

Structure visible in the Zn spectrum at approximately 2 eV below E_F, and in the Cd spectrum at

TABLE II. Valence-band data for cadmium. Summary of calculations and observations of electron energy-band structure for cadmium. The predominance of structure in the region of 10 eV below the Fermi level appears undisputable but only in two instances is a resolved structure reported and attributed to *d*-band structure.

Type of calculation/ experiment	Position of structure relative to Fermi level (eV)	Remarks	Ref.
Empirical pseudopotential	−8	Place *d* bands closely below bottom of *s*-*p* bands; included	13
APW	−17	Full Slater exchange: no dynamical corrections	14
APW	−8	$\frac{2}{3}$ Slater exchange: no dynamical correction; width ~ 2 eV	14
Plasma radiation	−9.1	Identified as volume plasmons or *d*-band structure	21
Soft x-ray spectroscopy	−10.4, −11.0	$4d_{3/2,5/2}$ doublet resolved	17
X-ray photoelectron spectroscopy (XPS)	−10	Single peak observed	24
Plasma resonance	−8168	Identified as plasma resonance	16
Characteristic energy loss	−7.5	Structure located at −7.5 and −15.1 eV; relatively poor resolution	22
Various	−9.3 ± 0.3	Survey up to 1967	23
XPS	−10.47, −11.46(± 0.09)	$4d_{3/2,5/2}$ doublet resolved	25
UPS (40.81 eV)	−10.2, −11.1 (± 0.1)	$4d_{3/2,5/2}$ doublet resolved	Present work

approximately 4.5 eV below E_F, is due to photoelectrons from the *d* bands excited by the 48.4-eV (256-Å) He$^+$ line which is present in our lamp with an intensity estimated to be $\frac{1}{20}$th of the intensity of the 40.81-eV (304-Å) resonance line.

DISCUSSION

A number of band-structure calculations for both Zn and Cd using a variety of computational techniques have appeared in the literature,[10,11–14] and reasonable agreement on the details of the *s*-*p* bands and on the Fermi-surface parameters has been obtained.[14] The two elements are isoelectronic in their outer shell configurations, but the positions of the *d* bands in both elements are particularly sensitive to details of the potential used in the calculations, and wide variations have occurred in the theoretical predictions as may be seen from Tables I and II. Recent Korringa–Kohn–Rostoker calculations for Zn have succeeded in more closely locating the position of the *d* bands.[10] Using 5/6 Slater exchange, Segall places the center of the band at − 8.5 eV below E_F, a value which rises to − 10.4 eV when full Slater exchange is included. It is hoped that the present results may help to refine these calculations even further.

The effect of crystal-field splitting of the $4d_{3/2,\ 5/2}$ levels of Cd is clearly shown by the present measurement of the peak separation (0.95 eV) when compared with the free-atom relativistic–Hartree–Fock–Slater calculation estimate[26] of 0.78 eV, and with the atomic-emission spectroscopic value of 0.70 eV.[27] Pollak *et al.*[25] have recently studied the splitting of the $4d_{3/2,\ 5/2}$ levels in Cd by means of high-resolution XPS. Their value of 0.99 eV for the peak separation is in good agreement with the present determination, but there remains an unresolved difference of 0.3 eV in the absolute location of the structure relative to E_F.

The tables also show data from a variety of related optical- and electron-impact characteristic energy-loss experiments. The latter are sensitive both to collective oscillations (volume and surface plasmons) and to density-of-states structure, as also are bulk reflectance measurements; and the interpretation of such experiments may be expected to be difficult whenever the plasmon energy is close to the energy difference between *d*-band structure and E_F. On the other hand, the plasma resonance experiment of Feuerbacher and Fitton[16] is thought to be sensitive only to collective oscillations, and the present experiment and those involving soft x-ray absorption and XPS should respond only weakly to plasmon generation.

The data on Cd in Table II would therefore suggest that the *d*-band structure centered at 10.68 eV below E_F, as determined by the present work, is clearly separated from the volume plasmon energy which is found by Feuerbacher and Fitton[16] to be 8.68 eV. A high-resolution characteristic energy-loss experiment would, however, be useful as additional confirmation of this assignment.

Data on Zn is considerably more extensive but less conclusive. The position of the *d* bands found in the present experiment lies between the value obtained by soft x-ray spectroscopy (10.6 eV)[17] and that obtained in an early electron spectroscopy for chemical analysis (ESCA) determination by Nording[18] (8.9 eV) and agrees closely with a recent measurement using 21.22-eV ultraviolet photoelectron spectroscopy by Nilsson and Lindau (9.5 eV).[19] In an earlier UPS measurement performed with low-energy photons ($\hbar\omega \leq 10$ eV), Mosteller *et al.*[28] claimed that a decrease in photoelectron yield between $\hbar\omega = 9.32$ and 9.54 eV, together with indirect evidence of an increase in the transparency of Zn at this energy, was indicative of the onset of plasma oscillations. The evidence of the present results suggests that this decrease in yield results rather from the onset of transitions of photoelectrons from the *d* states to states just above the Fermi level, from which emission is prohibited by the work function of the sample. Similarly, it appears that the abrupt change in the optical reflectance of Zn observed by Mosteller and Wooten[20] at 9.46 eV is also due primarily to the onset of photoelectric transitions from the *d* states. A plasma-radiation experiment performed by Herickhoff *et al.*[21] indicated a shoulder rather than a peak in the optical emission of electron bombarded zinc at a photon energy of approximately 8.6 eV. This result would also be directly interpretable in terms of the *d*-band location as reported here.

The results of a plasma-resonance experiment by Feuerbacher and Fitton,[16] while somewhat inconclusive in the case of zinc, are not presently explicable on the basis of emission from *d* states. The exact agreement in energy between the location of the resonance in photoelectron yield observed by Feuerbacher and Fitton and that of the *d*-band structure found in the present work, coupled with the fact that no energy dispersion (with angle of incidence of *p*-polarized radiation) was observed, would, however, suggest that the resonance may be due to features of the photoemission process other than those associated with plasmon decay. Alternatively, it must be assumed that the plasmon energy and *d*-band depth below E_F are identical in zinc.

CONCLUSIONS

The location of *d*-band structure in zinc and cadmium has been determined with high precision by means of ultraviolet photoelectron spectroscopy using 304-Å radiation, thereby demonstrating the particular advantages of this technique for band-structure studies. By comparison with other spectroscopic techniques it is concluded that the energy difference between the *d*-band structure and the Fermi level is similar to the volume plasmon energy in both materials, leading to difficulties in the interpretation of optical and of characteristic energy-loss experiments.

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Azbel'-Kaner Cyclotron Resonance at Far-Infrared Frequencies: General Theory and Experiments on Ga

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A general semiclassical expression is developed in the Azbel'–Kaner geometry for the resonant part of the surface impedance of a metal in the small-signal limit, with diffuse surface scattering, for an arbitrary ratio between typical orbit dimensions and skin depth. The expression is specialized to the case where the orbits are piecewise circular with constant velocity, as in the Harrison nearly-free-electron construction of the Fermi surface, and to the case of free electrons with an anisotropic mass tensor. For the latter case, the expressions are further specialized to the local limit for an ellipsoidal and a cylindrical Fermi surface, and it is shown that the surface scattering plays a significant role even in the local limit. The theoretical expressions for the surface impedance are compared with experimental results for a resonance in Ga at microwave frequencies and at the far-infrared frequencies 891 and 2530 GHz. It is shown that at microwave frequencies the subharmonic structure originates solely from the spatial inhomogeneity of the electromagnetic field, as in conventional Azbel'–Kaner cyclotron resonance, whereas at the laser frequencies the dominant source is the orbital anisotropy.

I. INTRODUCTION

The classical theory for Azbel'–Kaner cyclotron resonance[1] (AKCR) considers an electron moving in an orbit whose spatial extension, characterized by the orbit "radius" R_c (see Fig. 1), is large compared to the electromagnetic skin depth δ. Further, it is assumed that the duration of each traversal of the skin layer is short compared to the period of the electromagnetic field. For a general orbit these conditions can be written as

$$R_c/\delta \gg 1, \tag{1}$$

$$\omega(\rho_c\delta)^{1/2}/v_0 \ll 1, \tag{2}$$

respectively, where ρ_c and v_0 are the real-space radius of curvature and the Fermi velocity, both evaluated at the top point of the orbit, and ω is the applied frequency. For a free electron the two conditions are identical at the fundamental resonance $\omega = \omega_c$, and by inserting free-electron parameters one finds that both are comfortably satisfied at microwave frequencies. Going to lower magnetic fields, i.e., to the higher-order subharmonics, will make Eq. (1) better satisfied, whereas Eq. (2) will eventually be violated. However, for a free electron at microwave frequencies this will not happen until around the fiftieth harmonic. On the other hand, increasing the frequency will gradually lead to violation of both conditions due to the proportionate increase in magnetic field .

For a general orbit there is no definite relation between R_c and ρ_c, and the two conditions are thus independent. In particular, it is possible in many metals to find orbits which are free-electron-like on large parts, but which have much smaller overall dimensions and a much smaller mass than a free electron. In such a case, condition (2) may be violated at the fundamental resonance, even at microwave frequencies, whereas (1) is still well satisfied. This situation was studied in a recent publication[2] and it was verified that the breakdown