tion. If so, the small ionic radius of Li^+ lends support to Känzig's interpretation of a V_K center associated with a cation vacancy. Comparison of bond angles (Table I) indicates that the molecule-ion of the V_F center in LiF is more strongly perturbed by association than the molecule-ion of the lithium V_{KA} center in NaF. A vacancy might be expected to produce a larger bond angle than a cation impurity. It is also interesting to note the near equality of the molecular-fluorine hyperfine constants for the two associated centers and to compare them with the values for the V_K center (Table I). The F_2^- bond length has apparently relaxed to nearly the same value for both the V_{KA} center and V_F center. Although the V_{KA}-center results appear to strengthen the V_F-center interpretation of Känzig's observations, they also make a more definite confirmation desirable.

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DENSITY OF STATES IN NICKEL*

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In order to understand ferromagnetism in a metal such as nickel, the experience of the past three decades has clearly shown the necessity of determining the electronic quantum states in these materials. In recent years, a number of calculations of the energy band structure of Ni have been made.[1-3] In general, these calculations have been restricted to paramagnetic Ni and have yielded results which suggest that the band structure of Cu[3-5] and that of Ni could be related via the rigid-band model. Several workers have used these calculations and the results obtained from Fermi surface measurements of Cu and Ni to make estimates of the positions and nature of the bands of ferromagnetic Ni.[6,7]

However, the lack of experimental data away from the Fermi surface has made it very difficult to check the validity of the approximations used in the various theoretical models. It is the purpose of this Letter to report an experimental determination of the density of states in Ni over an energy range of 17 eV made by means of photoemission studies. These results are discussed in terms of the density of states in Cu and the various theoretical models.

The use of photoemission to obtain information about band structure has been demonstrated recently by work on various semiconductors[8-11] and metals.[12,13] Vacuum phototubes provided with LiF windows having a high-energy cutoff at 11.6 eV were used. A McPherson monochromator was used for measurements in the vacuum ultraviolet. The other experimental techniques used in the present work have been discussed previously.[14] An attempt to lower the work function of Ni by placing approximately a monolayer of Cs on the surface resulted in the formation of a Ni-Cs alloy; for this reason, the results reported here are for Ni samples without Cs. Since experimental measurements indicated that more than 99% of the surface area had a work function of 5.0 eV, this value has been used in the analysis here.

Energy distributions have been obtained for photon energies from 6.0 to 11.8 eV. Although it is not possible to present all of these data

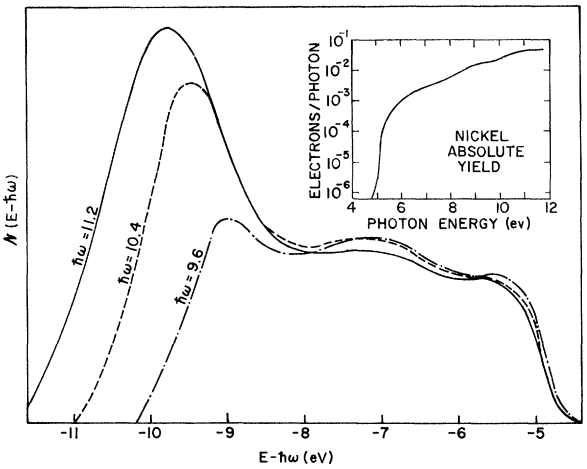

FIG. 1. Typical energy distributions $N(E-\hbar\omega)$ of photoelectrons from Ni. The exciting-photon energy is indicated on each curve. The curves have been referred to the initial states from which the electrons were excited by subtracting the exciting-photon energy $\hbar\omega$ from the measured kinetic energy E of the emitted electron. The insert gives the quantum yield. There is an uncertainty of ±30% in yeild between 8.0 and 9.8 eV.

here, typical curves are presented in Fig. 1. These curves have been normalized to the quantum yield so that for any value of $h\nu$ the ordinate is proportional to the number of electrons escaping with the energy E. The curves have also been shifted by the corresponding photon energies, $\hbar\omega$, to refer the distributions to the initial states of the photoemitted electrons.[10,13] (The zero of energy on this plot is the vacuum level.) The strong similarity of the structure in all of the distributions plotted in this way suggests that (1) nondirect transitions[15] (i.e. transitions in which conservation of $\vec{k}$ is not an important selection rule) dominate the optical transitions; (2) the matrix elements for each pair of optically coupled states are approximately equal; and (3) the energy distributions are essentially replicas of the valence-band density of states with approximately constant conduction-band density of states above the vacuum level. All of the energy distributions could be analyzed by a method derived from that of Kindig and Spicer.[16] The results of this analysis were in agreement with the suggestions listed above. The slight shifting towards lower energies of the peak near −5 eV in Fig. 1, and the loss of definition of the broad peak near −7 eV, as photon energy is increased, are believed to be due to inelastic scattering effects.[15] The strong peak near −10 eV is believed to correspond to a high-density peak in the valence-band density of states which is slowly uncovered as photon energy is increased. The valence-band density of states, N_V, derived from the energy-distribution curves is shown in Fig. 2(a). The detailed analysis indicates that the major contribution to the strong peak near −10 eV in Fig. 1 is due to valence-band structure, and that a smaller contribution is due to scattered electrons. The fact that the peak near −10 eV in Fig. 1 moves to higher energy with increasing $h\nu$ (it is located at $E=0.6$ eV for $h\nu=9.8$ eV, and at $E=1.7$ eV for $h\nu=11.8$ eV) is evidence independent of the detailed anal-

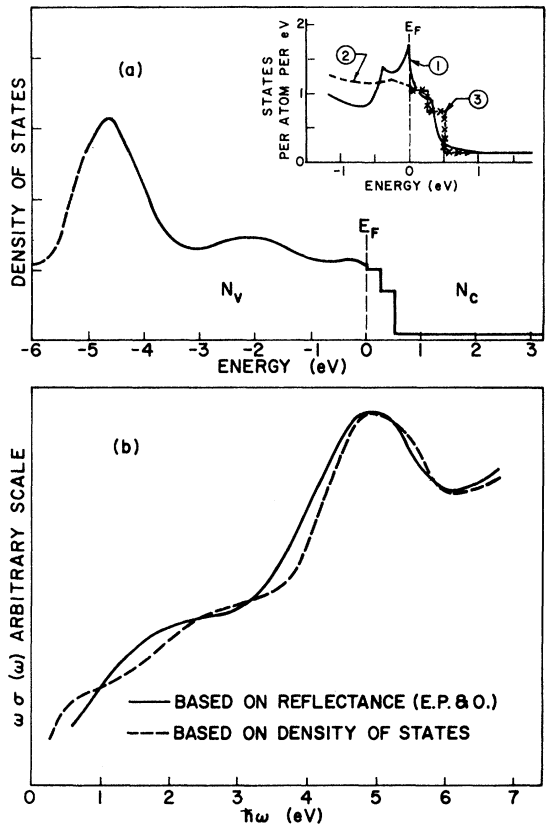

FIG. 2. (a) The density of states of Ni determined in this work. Since the conduction-band density of states was found to be approximately constant from 1 to 11 eV, the portion above 3 eV has not been shown. The insert compares the density of states near the Fermi surface found in this work (curves 2 and 3) with that (curve 1) determined using specific heat measurements in alloys.[17] (b) The optical constant $\omega\sigma$ determined from reflectance measurements[6] and from the results of this work. The curves have been normalized at 4.9 eV.

ysis[16] that this peak is due to a maximum in the valence-band density of states and not to scattering. The behavior of this peak in Ni should be contrasted with that of the peak due to scattering which appears at low energy ($E = 0.4$ eV) in Cu and Ag for $h\nu > 7.8$ eV, and stays at $E = 0.4 \pm 0.1$ eV independent of photon energy over a range of 4 eV or greater.[13] The first-order theoretical treatment of scattering by Berglund and Spicer[15] indicates that scattering should give a distribution which peaks at a constant (low) energy independent of $h\nu$. Because of the alloying problem, it was impossible to reduce the φ of Ni with Cs so that the motion of the peak could be followed over a larger energy range. However, a situation similar to that in Ni occurred for Fe where it was found that Cs could be applied without alloying. For uncesiated Fe, a low-energy peak appeared in the energy distributions for $h\nu > 10$ eV. This peak moved to higher energy with increasing $h\nu$; however, it could only be followed over a small range of $h\nu$. After Cs was placed on the surface of the Fe samples, it was possible to follow this structure over a range of almost 4 eV, and its position E was found to be given by $E = h\nu - 7$ eV.

Having determined the valence-band density of states N_V and that portion of the conduction-band density of states N_C which lies above the vacuum level, the density of states between the Fermi level and the vacuum level was then determined. This was done by recognizing the fact that the density of states of the d bands would be higher than that of the s- and p-like bands, and by assigning 0.6 empty state[17] to the high-density d-like states lying above the Fermi surface. It was assumed that the d-like band of states was continuous across the Fermi surface, and calculations of the optical conductivity were used to obtain the detailed shape of the empty portion of the d band. When nondirect transitions and constant matrix elements characterize the optical transitions in a material, the optical conductivity, $\sigma(\omega)$, is given by

$$\omega\sigma(\omega) = A\int_{E_F}^{E_F+\hbar\omega} N_C(E)N_V(E-\hbar\omega)dE,$$

where A is a constant which depends upon the constant matrix element and N_V is the valence-band density of states.[15] The closest agreement between the $\omega\sigma(\omega)$ calculated from this equation, using the valence-band density of states shown in Fig. 2(a), and that determined from the reflectivity data[6] was obtained with the conduction-band density of states shown in Fig. 2(a). The relatively high density of states observed in N_C within 0.5 eV of E_F is reasonable in view of the 0.6 empty $3d$-like states per atom in Ni.[17] The lower density above this region is believed to be due to empty s- and p-like states. The optical conductivity obtained from the reflectivity and that obtained from the density of states are shown in Fig. 2(b); these curves have been normalized at 4.9 eV. The agreement between the two curves is very good and strongly suggests that the strong peak near 5 eV in the optical conductivity is due to the high-density peak observed at -4.6 eV in the valence-band density of states. It should be noted that for $E > -4.6$ eV no structure was found in the valence band sufficiently strong to explain the maximum at 5 eV in $\sigma(\omega)$. The minor discrepancies between the two curves may be due to the assumptions in the model used here (any direct transition to states between the Fermi level and the vacuum level would not be included in this calculation), or due to the inherent difficulties in the Kramers-Kronig analysis used to determine $\sigma(\omega)$ from the reflectivity data.[6]

The density of states near the Fermi level derived from the energy-distribution curves and the optical conductivity is compared in the insert of Fig. 2 with that obtained from low-temperature specific heat studies of Ni and Cu and Ni-Cu and Ni-Fe alloys (curve 1), assuming the rigid-band model.[17] The amplitude of N_V derived from photoemission data (curve 2) has been set by arbitrarily assigning 10 electron states per atom to N_V [Fig. 2(a)] between -6 and 0 eV, and the amplitude of N_C derived using $\sigma(\omega)$ has been set by making curve 3 coincide with curve 1 for $E > E_F + 1.0$ eV. The agreement between the curves is encouraging. The discrepancy observed below E_F may be due to the crudeness of the rigid-band model assumed in the derivation of curve 1 and/or to the resolution limitations (0.1 to 0.2 eV near the Fermi surface) of the present experiment.

It is possible to examine the rigid-band model and to investigate the relationship between the density of states of nickel and copper through

the use of Fig. 2(a) and the Cu density of states, which was determined by Berglund and Spicer[13] and found to be in general agreement with that calculated by Burdick.[5] The Ni density of states from Fig. 2(a) is replotted in Fig. 3 (curve 1) along with the Ni density of states predicted from the Cu density of states[13] (curve 2) and the rigid-band model using an exchange splitting of 0.6 eV. To obtain the latter curve, five spin-up and five spin-down electron states were assigned to two bands having the same density of states as the bands observed in Cu. The two bands so obtained were then shifted in relation to each other by an amount of energy ΔE_d and summed; the Fermi level was determined by filling 9.4 of the ten d-like electron states.[17] The low-density s- and p-like states corresponding to the eleventh outer electron in Cu were not included in this calculation. A lower-energy peak in the Cu energy-distribution curves was observed by Berglund and Spicer, but not positively identified as being due to valence-band structure.[13] More recent information suggests that it is due to a maximum in the valence-band density of states.[18] As a result, the structure was added to the Cu density of states before curve 2 of Fig. 3 was derived.

The value of 0.6 eV for the exchange splitting, ΔE_d, was chosen as representative of values suggested in the literature.[19] It is clear from Fig. 3 that no matter what value of ΔE_d is chosen, the density of states of Ni cannot be obtained from that in Cu through the use of the rigid-band model.

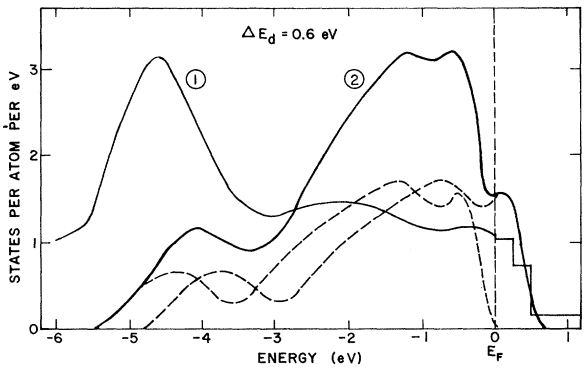

FIG. 3. The Ni density of states as determined from experiment in this work (curve 1). Curve 2 was constructed using the Cu density of states[13,18] and the rigid-band model with an exchange splitting ΔE of 0.6 eV. No value of ΔE could be found which would bring curve 2 into agreement with curve 1.

Once the rigid-band model is questioned, it is necessary to explain the observed differences between the densities of states in Cu and Ni. Since Ni is a ferromagnet and Cu is not, one might first guess that the observed differences are due to ferromagnetic effects; however, a number of pieces of data argue against such a simple explanation. First, a high-density band is found in Ni which is approximately twice as wide as the high-density band in Cu. The difference in bandwidth is approximately 3 eV, whereas the best present estimates of the exchange splitting in Ni are a few tenths of an eV.[19] Thus, the change in the width of the band structure in going from Cu to Ni is large compared to the energies usually associated with ferromagnetism. Second, preliminary studies of Ni above its Curie point (358°C) indicate no major differences between the densities of states in paramagnetic and ferromagnetic Ni.[20] Third, preliminary results of photoemission studies on paramagnetic Pd[21] indicate that its density-of-states curve is similar to that in Ni and quite dissimilar to that in Ag.[13] Fourth, studies of ferromagnetic Fe[20] indicate densities similar to those of Ni and Pd but quite different from those of Cu and Ag. For these reasons it appears that the major structural differences in the densities of states of Cu and Ni are not due to ferromagnetic effects.

The experimental data indicate that the band structures of Ni, Fe, and Pd are similar, but that as a group they are quite dissimilar to Cu and Ag. These data suggest that major portions of the band structures in these metals depend upon the number of s- and p-like electrons and upon whether or not the d-like band is filled. In Cu and Ag where the d band is filled, there is one s- and p-like electron per atom, whereas in Ni, Fe, and Pd, where the d band is only partially filled, there is on the average only about one-half of an s- or p-like electron per atom. These differences in electron configurations appear to give rise to new interactions which cause structure in the densities of states of these metals.[22] It appears that these interactions substantially affect the cohesive energies of transition and noble metals. Phillips has examined the spectral density of d-band metallic states in groups VIII (Ni, Pd, Pt) and IB (Cu, Ag, Au) in terms of resonant as well as band states.[22]

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POSSIBLE EVIDENCE OF DIPOLE-QUADRUPOLE INTERACTION IN As^{75}†

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This paper reports the observation of a structure in the photoneutron-production cross section of the spherical nucleus As^{75}, which may be ascribed to the interaction of the dipole and quadrupole vibrations.[1,2] The experimental cross section is compared with the theoretical cross section based on the dipole-quadrupole interaction model.

The experimental arrangement was essentially the same as that previously reported.[3] The monoisotopic As^{75} sample weighed about 105 g and was contained in a thin-walled glass container. The collimated bremsstrahlung beam from the electron synchrotron irradiated this sample placed along the beam axis at the center of a neutron detector made of 13.5-cm thick paraffin layers and eight BF_3 counters embedded in a ring concentric about the beam-sample axis. The paraffin thickness was chosen to make the neutron detection efficiency least sensitive to its energy.[4] The neutrons were counted during the 700-μsec gating period following a 20-μsec time delay between the beam pulse and the triggering of the gating circuit to prevent the electron pile-up pulses. The beam was monitored by a transmission ionization chamber, and the detection efficiency of the whole system was determined to be 2.5% using a calibrated Ra-Be source. X-ray picture studies of the beam size at the target position before and after the runs ensured that the target intercepted the whole beam throughout the experiment. The neutron-yield curves were constructed in 0.5-MeV intervals from 10 up to 25 MeV of bremsstrahlung energy. A total of twenty separate runs were made with the total counting statistics at the top energy point better than 0.3%. After correcting for the background, the average net yield per unit monitor response was computed at each energy, and the net-yield curve was analyzed directly through the Penfold-Leiss inverse brems-