VOLUME 33, NUMBER 22 PHYSICAL REVIEW LETTERS 25 NOVEMBER 1974

Local Density of States and Core-Hole Conduction-Electron Interactions in the X-Ray Photoemission Spectra of Pt and Ni

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(Received 22 July 1974)

The monochromatized x-ray photoemission spectra of the Pt $4f$ and Ni $2p_{3/2}$ levels in the pure elements exhibit an asymmetry which disappears when Pt and Ni atoms are diluted into Cd, but not when Pt is diluted into Au. From the behavior of the conduction-band photoemission spectra of these alloys it is argued that the elimination of the asymmetry is related to the reduction of the local density of states of the electrons at the Fermi level available to screen the hole potential, as suggested by recent theories.

It has long been recognized theoretically that in x-ray emission and in photoemission the hole potential can strongly influence the observed spectra.[1-8] Provided that the emitted electron does not strongly interact with those remaining in the solid, photoemission experiments measure the energy distribution of the hole states left behind. The validity of the interpretation of photoemission experiments in terms of one-electron band theory is determined by the nature of the distribution of hole states, or by the extent to which an electron can be removed without leaving a large number of excited electron-hole pairs behind. The least bound electrons observed in the photoemission spectra correspond to the completely relaxed hole state, provided that that state is not totally orthogonal to the initial state.[2] The excited electron-hole pairs coupled to the initial state by the hole potential give rise to a distribution of electron energies on the deep binding energy side of the main photoemission line.[4-8] Such excitations appear as discrete satellite lines on the core-level spectra of noble gases[9] and of transition-metal oxides.[10,11]

In metals having a high density of states at the Fermi energy, $N(E_F)$, the large probability of exciting many electron-hole pairs upon the removal of an electron can change significantly the shape of the core-level spectra.[1-8] It has been predicted that the readjustment of the Fermi sea to the hole potential and the subsequent creation of electron-hole pairs manifests itself as an asymmetric core-level line shape in the energy distribution of photoemitted electrons.[1-8] Recently, it has been shown experimentally that the core-level spectra of Ru, Pd, Ir, and Pt, which have a large $N(E_F)$, exhibit a noticeable asymmetry while those of Au and Ag, which have a small $N(E_F)$, exhibit essentially no asymmetry.[12]

Ferromagnetic and strongly paramagnetic metals are expected to show large core-hole effects, since they have a large $N(E_F)$ and strong electron-electron interactions. Presently, there is much controversy as to whether the failure of photoemission experiments to observe the exchange splitting[13,14] or the proper sign and magnitude of the spin polarization[15] in ferromagnetic materials is consistent with band theory.[16,17] It has been suggested that the influence of the hole potential is responsible for the disagreement between simple band theory and photoemission experiments.[18,19]

In spite of the fundamental importance of resolving the effects of the hole potential on the photoemission spectra of metals, experimental evidence has remained scarce. We report here an attempt to determine the influence of the core-hole potential on the core-level photoemission spectra by alloying metals having a high $N(E_F)$ (Pt, Ni) with metals having a low $N(E_F)$ (Au, Cd). These results show that indeed the core-level asymmetries are not an atomic effect, but depend on the local density of states at the Fermi level, verifying the above-mentioned theories.[4-8] The implication of the results is that in Ni and Pt, and other materials exhibiting core-level asymmetries, electrons cannot be removed without leaving behind a large distribution of excited low-energy electron-hole pairs. The interpretation of the photoemission spectra of the conduction bands of such materials must take into account the smearing effects of the excited electron-hole pairs.

The photoelectron spectra were measured on a Hewlett-Packard 5950 ESCA spectrometer. This instrument features a monochromatized Al x-ray source with dispersion-compensated electron optics, which together provide a resolution of 0.6 eV. The samples were prepared by cosputtering the pure metal targets at a rate of 10 Å/

sec in a pure (99.999%) argon atmosphere at 30 mTorr. The vacuum in the sample preparation chamber prior to sputtering was 2×10^{-7} Torr and in the analyzing chamber during the measurements it was 5×10^{-9} Torr. The solute concentrations, estimated from the strengths of the core-level peaks, were 9% for Ni in Cd, and 8% for Pt in Au and Pt in Cd. No contamination from carbon or oxygen was detected, except for Ni where approximately 3% of the measured atoms were oxidized. The agreement of the conduction-band spectra with those published previously[20] for clean Ni indicates that the oxide had little effect on them.

The core-level spectra of the Pt $4f$ spin-orbit-split doublet and the Ni $2p_{3/2}$ level in the respective pure elements, Pt diluted into Au and Cd, and Ni diluted into Cd are shown in Figs. 1(a) and 1(b). The corresponding spectra from the conduction bands are shown in Fig. 2. The binding energy scale for the core-level spectra is referred to the Fermi level of the pure elements. With respect to the Fermi level, the Ni $2p$ level in Cd is shifted by 0.4 eV and the Pt $4f$ levels in Au and Cd are shifted by +0.2 and − 0.5 eV, respectively. To facilitate their comparison, the core peaks of the dilute atoms have been aligned with those of the pure metal. The photoemission spectra reported for the pure metals are identical to those reported previously by others.[20,21] The shaded regions in Fig. 2 correspond to the density of states produced by the solute atoms, found by subtracting the contributions from the pure solvent elements. This procedure is accurate for Pt in Au only near the Fermi level since the very large Au density of states below 2 eV obscures any contribution from the Pt.

The core-level spectra of the pure metals in Fig. 1 display the asymmetry that several workers have attributed to the relaxation of the Fermi sea about the core hole.[1-7] The asymmetry appears to be somewhat larger for Ni than for Pt, possibly as a result of the larger density of states near the Fermi level, as shown in Fig. 2. The asymmetry is seen to disappear for Pt and Ni diluted into Cd, but is not affected when Pt is diluted into Au. It was also found that when Au and Cd are diluted into Pt, their core-level spectra remain as symmetric as in their pure metallic forms. These facts may appear to be inconsistent with theory since there is no direct relationship between the *total* density of states at the Fermi level and the occurrence of the asymmetries. We show in what follows how this apparent inconsistency can be removed.

Let us assume for the moment that the photo-

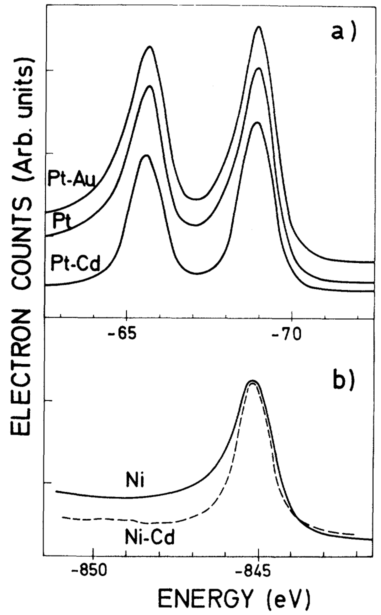

FIG. 1. Monochromatized x-ray photoemission spectra of (a) the Pt $4f$ level of pure Pt and Pt diluted into Au and Cd, and of (b) the Ni $2p_{3/2}$ level of pure Ni and Ni diluted into Cd.

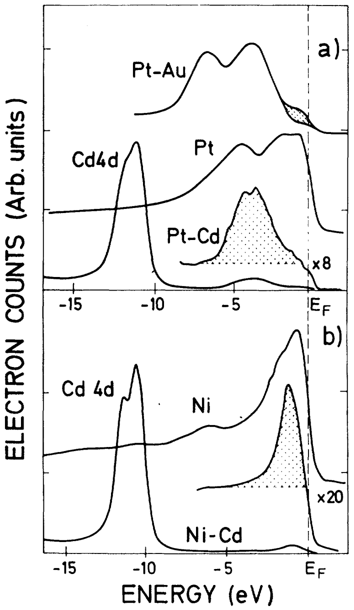

FIG. 2. Monochromatized x-ray photoemission spectra of the conduction bands of (a) pure Pt and Pt diluted into Au and Cd, and of (b) pure Ni and Ni diluted into Cd.

emission spectra of the conduction bands do give us an estimate of the single-particle electron density of states. These spectra show that the *local* density of states associated with the solute Pt and Ni atoms in Cd retreats from the Fermi level and becomes narrower than those of the pure solute metals. Subsequently the number of low-energy electron-hole pairs that can be produced in the excitation process is greatly diminished and the core-level asymmetry goes away. The Cd 4d levels are sufficiently far removed in energy and spatially localized so that they do not interact strongly with the d levels of the solute atoms. The d levels of the solute atom form virtual bound states in the Cd s-band continuum, accounting for their sharpening and pulling away from the Fermi level.[22] The retreat of the d level of the solute atoms from the Fermi level is surprising, since the charge filling the empty d levels would tend to shift them upward in energy, keeping them near E_F. If a total charge transfer took place so that the Ni and Pt atoms had electronic configurations like those of Cu and Au, the core levels would shift upward by several eV; the observed shifts in the core-peak positions are no more than ± 0.5 eV. If the s level of the solute atom becomes empty while the d levels become filled, no large charge transfer need take place. It is of interest to note that the core-level spectra of Pt diluted into Cd look similar to those of pure Au.[11]

At first, it is surprising that the asymmetry in the core-level spectra of Pt in Au does not disappear since the total density of states at the Fermi level is an order of magnitude less than in pure Pt. However, the situation in the conduction bands for Pt in Au is different from that for Pt in Cd. The Au d levels lie close in energy to the Pt d bands and have a similar spatial extent. Thus, the Pt d bands do not retreat from the Fermi level nor do they narrow significantly upon dilution in Au. The Pt d levels near E_F form virtual bound states in the Au s-band continuum that have a density of states nearly the same as in the pure Pt (as seen in Fig. 2) and thus the core-level asymmetry remains virtually unchanged.

Similarly, when Cd and Au are diluted into Pt and Ni the *local* density of states at the Fermi level of the solute atoms remains the same as in their pure metallic forms, even though the *total* density of states of the alloy at the Fermi level remains high. Thus, a hole state created on these solute atoms does not couple strongly to the large density of states of the solvent atoms and no detectable core-spectra asymmetries occur. This experimental fact proves that secondary electron-loss processes (e.g., plasmon excitations), which should be independent of the source of the electrons, are not responsible for the observed asymmetric line shapes of Ni and Pt. Since the solute Cd and Au atoms do not appear to couple strongly to the high density of states of the host, one can assume that the low-energy tail following their core-level spectra is due primarily to electron losses, and not to the excitation process. We may thus use the loss tail from the solute atoms to remove the secondary electrons from the core-level spectra of the Ni and Pt atoms to obtain a more accurate picture of the core-excitation spectrum. We are currently evaluating this possibility.

The present results show that the core-spectra asymmetry is not an atomic effect, but depends upon the *local density of states at the Fermi level.* This we believe to be decisive evidence for the core-hole screening mechanism proposed earlier[1-8]: For pure Ni and Pt, and other materials having core-spectra asymmetries, an electron cannot be removed from a core level without leaving behind a large number of excited low-energy electron-hole pairs. Since this has been shown to be true for the core levels of these metals, it must also, to some extent, be true for the electrons removed from the conduction band, provided that the potential produced by the conduction-band hole is similar to that of a core hole. We might thus expect the conduction-band spectra to be a convolution of the one-electron density of states with the shape of the observed core-level excitation spectra. (Doniach,[7] however, argues that the recoil of the conduction electron greatly reduces the number of electron-hole pairs over that expected from the excitation of core electrons.) It should be noted that the conduction-band spectra of Au and Cu would look similar to those of Pt and Ni if they were convoluted with the shape of the asymmetric Pt and Ni core-level spectra.

In conclusion, these results clearly demonstrate the importance of the hole potential in the photoemission spectra of Pt and Ni, and possibly other materials having asymmetric core-level spectra. The interpretation of the conduction-band spectra in terms of single-electron density of states must be done with caution. Fortunately, it appears that the hole interaction does not completely obliterate features of the valence-band spectra, but only smears them a bit. This interaction can, however, be responsible for the disagreement between photoemission experiments and band theory found in ferromagnetic materials.[18,19]

The author is indebted to M. Cardona, S. G. Bishop, P. C. Kemeny, and R. M. Martin for their critical comments and to S. Hüfner for bringing this problem to his attention.

[1] G. D. Mahan, Phys. Rev. 163, 612 (1967).

[2] P. W. Anderson, Phys. Rev. Lett. 18, 1049 (1967).

[3] P. Nozières and C. T. De Dominicis, Phys. Rev. 178, 1092 (1969).

[4] B. I. Lundquist, Phys. Kondens. Mater. 9, 236 (1969).

[5] S. Doniach and M. Sunjic, J. Phys. C: Proc. Phys. Soc., London 3, 285 (1970).

[6] D. C. Langreth, Phys. Rev. B 1, 3898 (1970).

[7] S. Doniach, Phys. Rev. B 2, 3898 (1970).

[8] L. Hedin, *Electrons in Crystalline Solids* (International Atomic Energy Agency, Vienna, 1973), p. 665.

[9] D. P. Spears, H. J. Fischbeck, and T. A. Carlson, Phys. Rev. A 9, 1603 (1974).

[10] G. K. Wertheim and S. Hüfner, Phys. Rev. Lett. 28, 1028 (1972).

[11] G. K. Wertheim, H. J. Guggenheim, and S. Hüfner, Phys. Rev. Lett. 30, 1050 (1973).

[12] S. Hüfner, G. K. Wertheim, D. N. E. Buchanan, and K. W. West, Phys. Lett. 46A, 420 (1974).

[13] D. T. Pierce and W. E. Spicer, Phys. Rev. B 6, 1787 (1972).

[14] J. E. Rowe and J. C. Tracy, Phys. Rev. Lett. 27, 799 (1971).

[15] H. Adler, M. Campagna, and H. C. Siegmann, Phys. Rev. B 8, 2075 (1973).

[16] E. P. Wolhfarth, Phys. Lett. 36A, 131 (1971).

[17] N. V. Smith and M. Traum, Phys. Rev. Lett. 27, 1388 (1971).

[18] S. Doniach, in *Magnetism and Magnetic Materials—1971*, AIP Conference Proceedings No. 5, edited by C. D. Graham, Jr., and J. J. Rhyne (American Institute of Physics, New York, 1972).

[19] P. W. Anderson, Phil. Mag. 24, 203 (1971).

[20] S. Hüfner and G. K. Wertheim, Phys. Lett. 47A, 349 (1974).

[21] S. Kowalczyk, L. Ley, R. Pollak, and D. A. Shirley, Phys. Lett. 41A, 4551 (1972).

[22] P. W. Anderson, Phys. Rev. 124, 41 (1961).

Electronic Charge Densities and the Temperature Dependence of the Forbidden (222) Reflection in Silicon and Germanium*

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(Received 24 June 1974)

Using nonlocal pseudopotentials for silicon and germanium we are able to calculate the temperature dependence of the forbidden (222) reflection and we find it to be in excellent agreement with experiment. The accuracy of the pseudocharge density for the case of silicon is also examined and found to be in good agreement with recent x-ray experimental results.

Remarkable progress has recently been made in the measurement of charge distributions in crystalline silicon and germanium.[1-6] These exceedingly precise measurements, in the case of silicon, have allowed the valence charge density to be accurately determined for the first time.[5] Such measurements are, of course, of considerable value not only as a means of ascertaining the accuracy of band-structure calculations and the resulting wave functions, but as a means of better understanding the bonding process itself. In this context there has been much interest in determining the behavior of the valence charge density, and in particular the bonding electrons, as a function of temperature. By combining neutron and x-ray diffraction studies, Roberto, Batterman, and Keating[6] have been able to establish the temperature dependence of the "forbidden" (222) reflection in both silicon and germanium, and specifically, they have been able to determine the relative contributions to the forbidden reflection arising from the bonding electrons and from the anharmonic motion of the ion cores.

From a theoretical point of view, while the use of pseudopotentials has been well established in the calculation of charge densities, only recently has it been possible to compare the results directly with experiment. Such a comparison, in