PHYSICAL REVIEW
LETTERS

VOLUME 17 | 5 DECEMBER 1966 | NUMBER 23

OPTICAL DENSITIES OF STATES OF NICKEL, COBALT, AND PALLADIUM*

A. Y.-C. Yu and W. E. Spicer
Stanford Electronics Laboratories, Stanford University, Stanford, California
(Received 7 October 1966)

The optical densities of states of Co and Pd have been determined. As with the other 3*d* ferromagnetic metals, Ni and Fe, Co is found to have the "anomalous" peak about 5 eV below the Fermi level. No such peak is present in Pd.

A striking feature has been reported in the optical densities of states[1] of Ni[2] and Fe.[3] This is a large peak at about 5 eV below the Fermi level E_F. Neither band calculations nor extrapolations from the noble metals via the rigid-band model predict this "anomalous" peak. Optical densities of states of Co and Pd determined by the same photoemission technique used for Ni and Fe are reported here. The principal purpose of this investigation was to determine whether or not the "anomalous" peak found in Ni and Fe was characteristic of the 3*d* ferromagnetic materials; Co completes this series. Palladium, which is paramagnetic, lies directly below Ni in the periodic table, and from band theory, its electronic structure would be expected to be similar to that of Ni. Thus, if the "anomalous" peak is associated with ferromagnetism in the 3*d* transition metals, it should appear in Co but not in Pd.

Quantum yields and photoelectron energy distributions were measured over the available spectral range $5.5 \lesssim h\nu \leq 11.6$ eV. The measurement technique has been reported elsewhere.[4] Most of the measurements were done in a high-vacuum stainless-steel chamber which was continuously pumped by a Vac-Ion system to maintain pressure about 5×10^{-10} Torr during measurements. The metals studied (99.99% pure) were evaporated by an electron-gun evaporation source in the high-vacuum chamber on a copper substrate just before the measurements were made. Typical pressure during evaporation was about 8×10^{-8} Torr. A large number of samples formed in this manner were studied and the features reported here were found to be completely reproducible. In addition, we have studied samples cleaned by heating in vacuum and obtained results identical to those from evaporated films.

In the spectral range studied, the optical transitions were found to be predominantly nondirect so that the energy distribution curves (EDC) are given by[2,5]

$$N(E,h\nu) = CT(E)N_C(E)N_V(E-h\nu),$$

where C is the square of the matrix element of optical transition and is assumed to be constant here, $T(E)$ is the electron escape function, and N_C and N_V are conduction- and valence-band optical densities of states, respectively. Since the position of all strong structure in the EDC was found to move in energy with $h\nu$ and no structure was observed which was stationary in energy, it was concluded that the structure in the EDC was due to the filled states N_V. At large values of $h\nu$, the EDC of

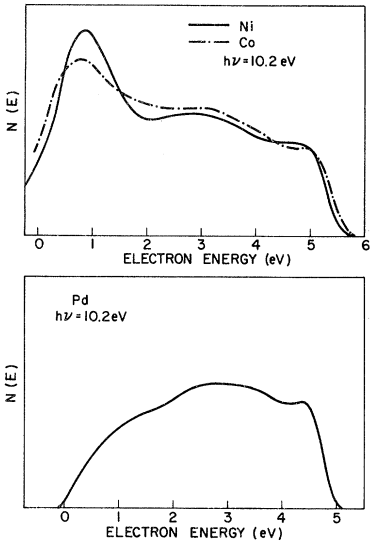

FIG. 1. Comparison of the photoemitted electron energy distribution curves at $h\nu = 10.2$ eV for Ni, Co, and Pd.

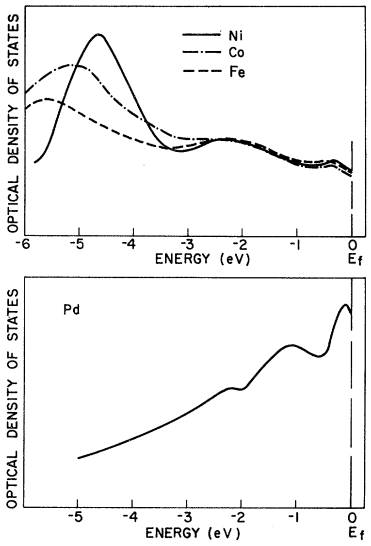

FIG. 2. Comparison of the optical densities of states of Ni, Co, Fe, and Pd.

Ni and Co are strikingly similar to each other, while being different from those of Pd. This is illustrated by Fig. 1, where EDC for Ni, Co, and Pd for $h\nu = 10.2$ eV are presented. These curves were traced from the recorder graphs; no corrections were made. Note the similarity between the EDC of Ni and Co. They both have gentle structure near 5 and 3 eV and a pronounced low-energy peak at about 1 eV. When we compare the EDC of Ni and Co with Pd, the most striking difference is the absence of this low-energy peak in Pd.

Using the equation above and the EDC, the optical densities of states of Co and Pd have been derived. These as well as the Ni and Fe optical densities of states are presented in Fig. 2. As would have been expected from the EDC of Fig. 1, both Ni and Co have a high peak at about -5 eV whereas no such peak is found in Pd. Thus, we conclude that this "anomalous" peak is indeed characteristic of the $3d$ ferromagnetic materials. No band calculations have predicted such a peak in either Ni, Co, or Fe, and it does not appear that the presence of this peak can be understood in terms of conventional band theory. There have been several interesting suggestions as to its origin. Phillips[6] has suggested that it might be due to a many-body resonance; Mott[7] has suggested that it might be due to the occurrence of a minority of Ni atoms with a d^8 configuration.

The data for Fe, Co, and Ni also bear on the rigid-band model. The optical densities of states for the complete range -3 eV $\leq E - E_F \leq 0$ in Ni and Co are similar and cannot be related by moving the Ni Fermi level downward to obtain the Co or Fe density of states as the rigid-band theory would predict.

In contrast to Ni, Co, and Fe, the Pd results seem to be in agreement with the expectation of band theory. The optical density of states of Pd is, to the first approximation, in agreement with the density of states predicted from the recent band calculations.[8] Also, the Pd optical density of states seems to be closely related to that[9] of Ag if the rigid-band model is applied. The sharp peak just below E_F is in agreement with the model proposed by Shimizu, Takahashi, and Katsuki[10] to explain the electronic specific heat and magnetic susceptibility data.

From this systematic study of the transition metals, it is concluded that the optical density of states varies strikingly between ferromagnetic and paramagnetic metals. The $3d$ ferromagnetic metals are found to have similar optical densities of states with an "anomalous" peak about 5 eV below the Fermi level. No such peak is found for $E - E_F > -6$ eV in Pd,[11] suggesting that it is probably related to the ferromagnetism of the $3d$ transition metals.

*Work supported by the Advanced Research Projects Agency through the Center for Materials Research at

Stanford University, and by the National Science Foundation.

[1]The density of states obtained from optical data (photoemission and reflectivity data) is called the optical density of states. See W. E. Spicer, to be published.

[2]A. J. Blodgett and W. E. Spicer, Phys. Rev. 146, 390 (1966).

[3]A. J. Blodgett and W. E. Spicer, to be published; W. E. Spicer, J. Appl. Phys. 37, 947 (1966).

[4]W. E. Spicer and C. N. Berglund, Rev. Sci. Instr. 35, 1665 (1964).

[5]W. E. Spicer, Optical Properties and Electronic Structure of Metals and Alloys (North-Holland Publishing Company, Amsterdam, 1966), p. 296.

[6]J. C. Phillips, Phys. Rev. 140, A1254 (1965).

[7]N. F. Mott, Optical Properties and Electronic Structure of Metals and Alloys (North-Holland Publishing Company, Amsterdam, 1966), p. 314.

[8]A. J. Freeman, J. O. Dimmock, and A. M. Furdyna, J. Appl. Phys. 37, 1256 (1966).

[9]C. N. Berglund and W. E. Spicer, Phys. Rev. 136, A1044 (1964).

[10]M. Shimizu, T. Takahashi, and A. Katsuki, J. Phys. Soc. Japan 18, 240 (1963).

[11]Although a peak at about −5 eV does not exist in the optical density of states of Pd, the possibility that an anomalous peak is present at lower energies cannot be ruled out. Optical reflectivity data seem to suggest the presence of such peak at about −7 eV. Experiments to probe this deep state by photoemission are under way.

REMOVAL OF SINGLE INTERSTITIALS FROM IRRADIATED PLATINUM*

J. M. Galligan
Columbia University, New York, New York

and

M. J. Attardo
Brookhaven National Laboratory, Upton, New York

(Received 13 October 1966)

A variety of indirect experiments have been undertaken to establish specifically what defects give rise to specific annealing stages in irradiated, quenched, and deformed crystals.[1] The goal of such a program—aside from technological aspects—is to gain a quantitative understanding of the energetics of formation, motion, and interaction of the crystalline defects involved. In many instances the activation energies obtained from annealing experiments on irradiated, quenched, or deformed crystals have not allowed a critical distinction to be made among the possible defects thought to be present in such experiments. This is especially true in the large number of studies that have been performed on copper and gold.[2] In this sense platinum presents a somewhat simpler situation,[3] since stages III and IV do not overlap and quenching experiments are quite well catalogued.[4] We have undertaken some direct observations, using field-ion microscopy,[5] of the removal of single interstitials from neutron-irradiated platinum in stage III, which are reported here.

This experiment was performed in the following manner: High-purity platinum wire (99.9998% pure obtained as special lot material from Englehardt Industries, Inc.) 2 mils in diameter was annealed at 1200°C for 48 h in vacuum of 10^{-7} Torr. The annealed wire was then irradiated to an integrated neutron flux of 10^{18} nvt ($E \geq 1.45$ MeV) in two batches—one at 100°K and the other at 340°K, which are temperatures above and below stage-III recovery in this material.[3] Specimens were electrolytically shaped in a KCN bath for examination in a field-ion microscope, from the material irradiated at the two temperatures, with the following precautions. In the case of the material irradiated at low temperatures, electropolishing was carried out at temperatures below 280°K and specimens transferred to a field-ion microscope which was cooled down to 78°K, all in a maximum of 10 to 12 min. An estimate of the extent of annealing that would have occurred in this time interval, using Bauer and Sosin's annealing data for irradiated platinum, gives a maximum of 30% recovery. In any case the material has not fully recovered in stage-III recovery. For the material irradiated at 340°K no such precautions were necessary in preparation of the specimens.

The observation of interstitials in a field-ion microscope depends upon the enhanced field at a protrusion due to the bulging out of atoms at a surface caused by a subsurface interstitial,