Photoemission Investigation of the Electronic Structure of Dysprosium*

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Photoemission measurements in the spectral range from the threshold ϕ at 3.2 eV to 11.8 eV have been obtained from evaporated films of dysprosium. The energy distribution of the emitted electrons and the quantum yield were measured at room temperature and below the magnetic-ordering temperatures. The optical transitions are predominantly nondirect and temperature-independent. A high density of d-like states is observed near the Fermi energy (E_F) , with a peak at $E - E_F = -0.3 \pm 0.1$ eV and a shoulder at $E - E_F = 1.1 \pm 0.1$ eV. The width of the s- and d-like filled states is 5.5 ± 0.2 eV. These observations are in very good agreement with recent band calculations. No structure is observed in the empty states for $E - E_F > 4$ eV. The emission of inelastically scattered electrons is observed in the energy distributions and their contribution to the measured distribution is estimated with a simple model. The scattering is attributed to contamination of the sample by residual gases in the vacuum. As a result of the scattering effects, only an estimate of the optical density of filled states is obtained for $E - E_F < -2.0$ eV. As a sample ages, an additional peak appears in the energy distributions at $E - h\nu + \phi = 2.7 \pm 0.1$ eV, and it is attributed to emissions from states produced by sample contamination. Structure in the energy distributions is also observed at $E - h\nu + \phi = 6.3 \pm 0.2$ eV. The possibility that the latter structure is due to f states is discussed. The data obtained at temperatures below the magnetic-ordering temperatures show no measurable effect. Thus, shifts due to magnetic ordering in the filled density of states are less than 0.3 eV. As expected, the general properties of the optical density of states for dysprosium are very similar to those obtained for gadolinium.

I. INTRODUCTION

ATA from photoemission experiments in the spectral range from 3.2 to 11.8 eV are used to study the electronic structure of dysprosium. Data are obtained at room temperature and below the magnetic ordering temperatures. Photoemission experiments have also been used recently to study various classes of metals.^{1,2} The only other rare-earth metal that has been studied is gadolinium.³⁻⁶ Properties of the rare-earth metals that are particularly interesting are their ordered magnetic states and the energy of the f electrons.

The experimental techniques and data obtained are presented in Secs. II and III, respectively. The data are analyzed and the optical density of states⁷ is obtained in Sec. IV. Section V is a discussion of the results. Good agreement is found between the data and recent band calculations. The results are compared to those obtained for Ga. Structure is also observed that is associated with surface contamination. The possible observation of felectron states is discussed.

II. EXPERIMENTAL PROCEDURE

The photoemission measurements were made on evaporated films of Dy in an all-metal vacuum chamber. The measurements give data on the energy distribution of emitted electrons and the quantum yield. Since the important features of the techniques have been described elsewhere, only a summary is presented here. The experimental ultra-high-vacuum chamber and photodiode assembly design have also been discussed previously.2 Briefly, the 4-in. stainless-steel chamber is pumped with a 15-liter/sec sputter-ion pump mounted directly on the chamber. The elements of the photodiode are attached to electrically insulated Dewars. The exciting radiation from a one-meter normal-incidence monochromator passes through a LiF window which is sealed with AgCl.

The energy distribution curves (EDC's) for the photoemitted electrons are measured by taking the derivative of the retarding potential curve (current versus voltage). Two techniques were used: (1) ac modulation of the current,8 and (2) operational-amplifier differentiation of the current obtained with a Carv Model 401.9 The latter technique was used for the greater part of the measurements. The differentiator was typically operated with a resolution of 0.15 eV. Typically a 4-Å monochromator band-pass was used.

The samples were formed by vacuum depositions from a Dy ingot in a tungsten-cloth basket. The small basket was resistance-heated and placed inside the photodiode so that both elements of the photodiode were covered.

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¹ A. Y-C. Yu and W. E. Spicer, Phys. Rev. 169, 4967 (1968), and references cited therein.

² G. J. Lapeyre and K. A. Kress, Phys. Rev. 166, 589 (1968), and

 ⁶ J. Lapere and K. A. Kress, Flys. Rev. 100, 389 (1908), and references cited therein.
 ⁸ A. J. Blodgett, Jr., W. E. Spicer, and A. Y-C. Yu, *Optical Properties and Electronic Structure of Metals and Alloys* (North-Holland Publishing Co., Amsterdam, 1966), pp. 246–256.
 ⁴ A. J. Blodgett, Jr., Ph.D. thesis, Stanford University, 1967 (uppublished)

⁽unpublished). ⁶ A. Y-C. Yu, Ph.D. thesis, Stanford University, 1967 (unpublished).

⁶ D. E. Eastman, Bull. Am. Phys. Soc. 13, 486 (1968); and (private communication).

The density of electronic states obtained from optical experiments. See W. E. Spicer, Phys. Rev. 154, 385 (1967).

⁸ W. E. Spicer and C. N. Berglund, Rev. Sci. Instr. 35, 1665

^{(1964).} ⁹K. A. Kress and G. J. Lapeyre, Rev. Sci. Instr. 40, 74





FIG. 1. The spectral dependence of the quantum yield (electrons per incident photons) of Dy. The insert is the determination of the work function and value obtained is 3.2 eV.

III. DATA

A. Quantum Yield

The quantum yield obtained by measuring the light flux against freshly prepared sodium salycilate² is shown in Fig. 1. The quantum yield is not corrected for the reflectance and is given in terms of electrons emitted per incident photon. The yield measurement requires knowledge of the transmission of the LiF window used on the experimental chamber. The window transmission was observed to degrade with time, due to exposure to the monochromator vacuum. The exposure time between the yield measurement and the window measurement was minimized. The degradation may introduce some error into the yield determinations, particularly at higher photon energies. The absolute value of the yield was measured with a calibrated nitric-oxide NO chamber at $h\nu = 10.2$ eV.¹⁰ The absolute measurement of the yield





¹⁰ The chamber was obtained from Melpar, Inc., Falls Church, Va. See A. K. Stober, R. Scolnik, and J. P. Hennes, Appl. Opt. 2, 735 (1963).



FIG. 3. Energy distributions of photoemitted electrons from Dy plotted versus $E - h\nu + \phi$ for $h\nu = 7.0-10.0$ eV. The curves are normalized to the quantum yield.

may be in error by as much as 20%. The quantum yield does not contain any strong structure. The maximum yield is small, which is typical of measurements on transition metals.^{1,2}

The work function ϕ is determined by plotting the half-power of the yield as a function of photon energy. The curve is shown in the insert in Fig. 1 and the value 3.2 eV is obtained. The linear dependence near threshold is predicted by the Fowler theory.^{11,12}

B. Energy Distribution of Photoemitted Electrons

A representative set of EDC's are shown in Figs. 2-4. The EDC's are plotted as a function of $(E-h\nu)+\phi$, where *E* is the kinetic energy of the emitted electron. The rationale for displaying the data in this manner will be presented in the next section. The EDC's shown in Figs. 3 and 4 are normalized to the quantum yield shown in Fig. 1. This is a reasonable procedure because the reflectance of Gd,^{3,5} a metal very similar to Dy, is approximately constant in the spectral range from 7.5 to 11.5 eV. This is not true, however, for the spectral range below 7 eV. Thus the EDC's shown in Fig. 2 have arbitrary amplitudes.

The set of EDC's shown in Figs. 2–4 were obtained before the film was 36 hours old. Comparison of EDC's obtained when the film was less than an hour old to ones obtained after aging two days showed no major changes. The ratio of the low-kinetic-energy (KE) peak to the high-KE peak for $h\nu$ greater than 11 eV increases by a few percent and the work function decreases slightly; by approximately 0.05 eV.

The dominant feature of the EDC's is the strong and structured peak near the maximum kinetic energy in the distributions. As the photon energy increases the shape of the peak changes. This is attributed to electrons being inelastically scattered out of the distribution and is typical of metallic studies.^{1,2} At the higher photon

¹¹ C. N. Berglund and W. E. Spicer, Phys. Rev. **136**, A1030 (1964); **136**, A1044 (1964).

¹² R. H. Fowler, Phys. Rev. 38, 45 (1931).

energies, the two structures in the high-KE peak become more evident. The position of the two structures labeled 1 and 2 in Figs. 2-4, occur at $(E - h\nu) + \phi = -0.3 \pm 0.1$ eV and $(E-h\nu)+\phi=-1.1\pm0.1$ eV. If the high-KE peak did not have structure, its maximum would be altered uniformly by the scattering effects. The measured EDC's, however, do not exhibit the latter property (see Fig. 3). Other major features observed in the EDC's are a slight minimum at $(E-h\nu)+\phi=-5.5$ ± 0.2 eV and a peak at $(E-h\nu)+\phi=-6.3\pm0.2$ eV. The latter two structures are labeled 3 and 4, respectively, in Figs. 3 and 4.

C. Comparison of Data from Various Samples

Five Dy samples were studied. The comparison of the EDC's obtained for these samples is shown in Fig. 5. Sample B was studied in a tipped-off glass tube which was evacuated with an ion pump.¹³ The sample was prepared before the tube was taken from the pump. Samples C, D, and E were studied in the continuously pumped metal chamber described in Sec. II. The relative amplitudes of the EDC's in Fig. 5 are arbitrary. Two features of the data are noted. First, the number of low-KE electrons with respect to the number of high-KE electrons shows considerable sample dependence. Second, the high-KE side of the first maximum in the EDC's is attenuated more than the low-KE side for the curves which have larger numbers of low-KE electrons. The maximum chamber pressure was approximately 5×10^{-8} , 7×10^{-9} , and 1×10^{-8} Torr during preparation of samples C, D, and E, respectively. After sample preparation the chamber pressure dropped below 1×10^{-9} Torr. Pressures were determined from the ion pump current. This should be a good measurement because the pump is attached directly to the chamber. The differences in the data obtained from these samples are attributed to inelastic scattering due to contamination. The contamination of the samples is considered to be principally at the surface¹⁴ and due to the residual gases



FIG. 4. Energy distributions of photoemitted electrons from Dy plotted versus $E - h\nu + \phi$ for $h\nu = 10.5 - 11.8$ eV. The curves are normalized to the quantum yield.



FIG. 5. Energy distributions of photoemitted electrons from four Dy samples for $h\nu = 8.5$ and 11.5 eV. The curves have arbitrary amplitudes, and are plotted versus $E - h\nu + \phi$.

in the vacuum chamber. Similar scattering effects due to sample contamination have been observed in the investigation of Gd.4,6 Extension of the above observations implies that a large fraction of the low-KE electrons in sample D also result from scattering by sample contamination. The additional structure observed in sample C is discussed in the next section.

D. Aging Effects

The EDC's for sample C in Fig. 5 show an additional peak not observed for samples D and E. The EDC's shown were obtained when sample C was about 5 days old. (The peak was also present at one day.) Data ob-



FIG. 6. Energy distributions of photoemitted electrons from Dy plotted versus $E - h\nu + \phi$ for $h\nu = 8.5$ and 11.5 eV. The curves were obtained when the sample was one day and thirty-eight days old. respectively, and the amplitudes of the curves are arbitrary.

¹³ G. J. Lapeyre, Bull. Am. Phys. Soc. 11, 251 (1966).
¹⁴ The term "at surface" is used since the impurities may diffuse into the metal.



FIG. 7. Energy distributions of photoemitted electrons from Dy at room temperature and liquid-air temperature for $h\nu = 8.5$ and 11.5 eV. The relative amplitudes at each photon energy are not arbitrary, but the absolute amplitudes of the curves are arbitrary.

tained from sample C at 25 days show the structure under consideration to be much larger, with no significant increase in width. There is no evidence for this structure in the data obtained from samples D and E when they were a few days old. Data were obtained, however, from sample D 38 days after preparation, and the same structure was observed. The aging effect for sample D is shown in Fig. 6. The peak position for the additional structure has a fixed value for $(E-h\nu)+\phi$ $=2.7\pm0.1$ eV. The relative amplitudes of the EDC's in Fig. 6 are arbitrary. Note that the aged EDC's in Fig. 6 show more scattering effects, i.e., a larger number of low-KE electrons and attenuation of the high-KE electrons. Sample B, studied in a tipped-off tube, shows a very broad peak in the KE region of the aging peak observed in samples C and D. Sample B did not develop a peak with age.

E. Temperature Dependence

Studies of photoemission as a function of temperature were made on samples C and E. The EDC's obtained at room temperature and liquid-air temperature for sample C are shown in Fig. 7. The relative amplitude of the curves at the same photon energy are significant, and thus the temperature dependence of the yield is obtained. The only difference in conditions for the two EDC's at $h\nu = 11.25$ eV was the addition of liquid air to the Dewars holding the diode. The low-temperature curve at $h\nu = 8.5$ eV was obtained by reproducing the experimental conditions used to obtain the room temperature curve. The differences in the curves are not

greater than the accuracy of the measurements.¹⁵ Lowtemperature EDC's obtained on sample C essentially superimpose the room-temperature EDC's. Since the Curie temperature¹⁶ (85°K) for Dy is near liquid-air temperature, heat was applied to sample C, and the data were obtained at about 10° above liquid-air temperature. Measurements were also made below the boiling point of liquid air by pumping until it froze. The data obtained above and below the Curie temperature show no measurable temperature dependence.

IV. OPTICAL DENSITY-OF-STATES ANALYSIS

A. Model Used for Analysis

In anticipation of the analysis of the data, the EDC's (Figs. 2-4) were displayed as a function of $(E-h\nu)+\phi$. The essential superposition of the EDC's when displayed in this manner indicates that the only important selection rule for the optical transitions is energy conservation. In cases where photoelectric emission data show this character the optical transitions are said to be nondirect.11,17 The temperature studies (discussed in Sec. V) show that the optical transitions are not phononassisted, and thus that they differ from indirect transitions.²

In the nondirect-transition model, the energy distribution of the emitted electrons at a given photon energy is related to the optical density of states (ODS) by the following equation^{11,18}:

$$N(E) = CT(E)N_{c}(E)N_{v}(E-h\nu)S_{0}(E) + S_{I}(E), \quad (1)$$

where N_{v} is the valence (filled) band ODS and N_{c} is the conduction (empty) band ODS. T(E) is the escape function and C is a constant which contains the squared matrix element for the transitions. The matrix elements are assumed to be constant, and the analysis shows the assumption to be reasonable. Metallic data frequently exhibit this property.^{1,2} The term $S_0(E)$ accounts for the electrons that have been inelastically scattered out of the EDC, and the term $S_I(E)$ represents the electrons inelastically scattered into the EDC (secondaries). [The photon energy is a parameter in Eq. (1), since C, S_I , and S_0 are *hv*-dependent.] For intrinsic scattering, these two scattering effects have been discussed and examined analytically in the literature.^{11,17,18} In addition to intrinsic scattering, however, one also has scattering due to bulk impurities and scattering due to impurities at the surface. The simple model for impurity scattering used in the analysis is presented in the Appendix.

¹⁵ The largest perturbation on the experiment is the contraction of the Dewars upon cooling; this probably accounts for the changes observed at zero KE, since the orientation of the diode changes with respect to the optical axis.

¹⁶ A spiral spin structure, with a transition temperature at 179°K, exists above the Curie temperature. ¹⁷ A. J. Blodgett, Jr., and W. E. Spicer, Phys. Rev. 146, 390

^{(1966).} ¹⁸ W. F. Krolikowski, Ph.D. thesis, Stanford University, 1967 (unpublished).

B. Method of Analysis

Examination of Eq. (1) shows that only the valenceband density of states has an $(E-h\nu)$ -dependence, and that the final density of states has an *E*-dependence. Since the structures observed in the EDC's depend on $E-h\nu$, the structures are in the valence band. The structures are indicated by the arrows 1-4 in Figs. 2-4. With respect to the Fermi energy, the energy of the valence-band structures is given by the numerical values on the energy axis in Figs. 2-4. No strong structure with *E*-dependence is observed in the EDC's. Therefore the conduction band above the vacuum level has no structure.

The relative shape of the valence band ODS is more difficult to obtain from Eq. (1). The data indicate that the emission of inelastically scattered electrons contributes significantly to the EDC's, particularly at higher photon energies. (See the discussion of the data in Sec. III C.) The greater part of the secondary emission is attributed to scattering by impurities probably in the surface region. A simple model, presented in the Appendix, is used to estimate the distribution of secondary electrons [the $S_I(E)$ term in Eq. (1)]. The result of the impurity-scattering model is very similar to that obtained for intrinsic scattering. Thus our inability to distinguish uniquely between the two scattering processes is not critical.

An approximate shape for the conduction band ODS is obtained in two steps. First, Eq. (1), neglecting $S_I(E)$, is used to find an uncorrected valence band ODS, N_V^+ . The analysis is performed by normalizing the family of EDC's as a function of $E - h\nu$ in the KE region near 2.25 eV.² The envelope that results from the procedure is the uncorrected valence-band ODS. The results are shown in curve one of Fig. 8. The data used in this analysis are those obtained from sample D. The above method of analysis compensates for the distortion of the EDC's by the electrons scattered out of the distribution. To examine the self-consistency of this analysis, the



FIG. 8. Estimates of the valence-band ODS for Dy. Curve 1 is uncorrected for secondary-electron effects and curve 2 is corrected for secondary-electron effects.



FIG. 9. The energy distributions divided by curve 1 of Fig. 8 shifted by the photon energy. The curves are normalized at E=2.5 eV.

EDC's are divided by $N_{\nu}^{+}(E+h\nu)$. The results of this division are shown in Fig. 9. The amplitudes of the ratios are arbitrarily normalized. The single curve at lower energy in Fig. 9 is formed by the superposition of all the resultant curves obtained in the above division. The variance in the superposition is less than 4%. At higher energies, however, the ratios diverge and they are a function of $h\nu$. The latter deviations are a result of the electrons that are inelastically scattered out of the EDC's $[S_0 \text{ term in Eq. (1)}]$. The consistency of the above divisions shows that the model used is essentially correct and that the matrix elements for the transitions are approximately constant. The curve in Fig. 9 from 0 to 3.5 eV represents principally the product of the escape function and the conduction band ODS, $T(E)N_{c}(E)$ in Eq. (1).

Second, an estimate of the effects due to the emission of the inelastically scattered electrons on the ODS analysis is made by calculating the distribution of secondaries. The calculations and the simple model used to obtain them are presented in the Appendix. The result of the correction is shown as curve 2 in Fig. 8. The correction alters the relative shape of the ODS for $E-E_F < -2$ eV, but does not change any major structures. The correction slightly shifts the position of the peak at the bottom of the ODS to higher energies.

The conduction-band optical density of states for $4 < E - E_F < 11.8$ eV contains no structure and is approximately constant. Two properties of the model give this result. First, no structure is observed in the EDC's with *E*-dependent positions. Second, the above analysis for the valence-band ODS is consistent with Eq. (1).

V. CONCLUSIONS AND DISCUSSIONS

A. ODS for $-5.5 < E - E_F < 0$ and $3.2 < E - E_F < 11$ eV

The photoemission data from evaporated films of Dy show that nondirect optical transitions dominate. The temperature dependence of the data shows that the transitions are not phonon-assisted (see Sec. V D). The



FIG. 10. Comparison of the estimated Dy ODS (corrected for scattering) with the calculated density of states of Keeton and Loucks (Ref. 19).

nondirect transition model with constant matrix elements is used to obtain an ODS. The emission of inelastically scattered electrons is observed in the EDC's and a major part of the scattering is attributed to sample contamination. A simple model has been used to estimate the distribution of secondaries, and corrections for the effects are made in the density of states analysis. The dominant feature of the valence-band ODS is the structured high density of *d*-like states near the Fermi level (see Fig. 8). The bottom of the s- and d-like states is given by the minimum at $E - E_F = -5.5$ eV. The structure observed below -5.5 eV in the ODS will be discussed in the next section.

The valence-band ODS incorporating the estimated effects of scattering is compared to theory in Fig. 10. The theoretical density of states is obtained from the band calculations of Keeton and Loucks.¹⁹ The over-all agreement of the two results is very good. The total widths of the experimental and calculated bands are 5.5 ± 0.2 and 5.4 eV, respectively. The calculated results have peaks at E_F and at 1.05 eV below E_F , which correlate with the peak 0.3 ± 0.1 eV below E_F and the shoulder 1.1 ± 0.1 eV below E_F in the ODS. The above features are found in the primary data, and their existence does not depend on the details of the analysis procedure [see the structures labeled 1, 2, 3 in the data (Figs. 2 and 3) and in the optical density of states (Fig. 10)].

The detailed shape of the valence-band ODS for $-5.5 < E - E_F < -2$ eV is only a first approximation, since it depends on the model used to estimate the emission of scattered electrons. The magnitude of the ODS in Fig. 10 is obtained by assigning three electrons per atom to the energy range $-5.5 < E - E_F < 0$. The major point of disagreement lies in the fact that the calculated density of states shows a minimum about

0.6 eV below the Fermi level. This is not observed in the experiments. The absence of this minimum in the experimental data can be accounted for by lifetimebroadening and electronic-relaxation effects.^{7,20} It is interesting to note that in the photoelectric data the two structures originating from the states near the Fermi level become more pronounced at the larger optical excitation energies where scattering is significant.

No strong structure is observed in the conductionband ODS above the vacuum level. The absence of any large density of states above the vacuum level implies that the empty *d*-like states occur at $0 \le E - E_F \le 4$ eV. The band calculations by Keeton and Loucks were not extended to energies above the vacuum level. Band calculations by Dimmock and Freeman for Gd,²¹ which is very similar to Dy (see paragraph below), have strong structure for $E - E_F > 4$ eV. (See Refs. 3 and 4 for a discussion of the Gd studies.)

Comparison of the results of these experiments with those on Gd^{3,4} shows good general agreement. Both metals show a high density of d-like states just below the Fermi level and essentially constant density of states above the vacuum level. (No structure in the *d*-like peak was observed in Gd.) The strong similarity between the density of states for the two metals is expected. The results of the band calculations by Keeton and Loucks show that the density of states for Dy and Gd are very similar. The Gd study shows a weak peak in the ODS at 2.6 eV below E_F . The latter peak is probably analogous to the aging peak observed in this study (see Sec. V C).

B. ODS for $E - E_F < -5.5$ eV

The low-energy peak in the valence-band ODS results from the maximum observed in the EDC's at $(E-h\nu)$ $+\phi = 6.3$ eV. The position of the peak in the data has an $(E-h\nu)$ dependence which is characteristic of occupied states. Thus, the peak is not attributed to emission resulting from simple electron-electron scattering, because this type of scattering produces a peak in the EDC's with an E-dependence very near zero kinetic energy.11,17,20 The peak, however, is superimposed on a large number of secondary electrons so that the magnitude and detailed shape of the structure is difficult to evaluate. Several possible interpretations are presented. The scope of the present data, however, is not sufficient to make a definitive interpretation.

First, the low-energy peak could be due to *f*-electron states. Similar structure has been observed in Gd at a slightly higher energy and has been interpreted as due to f states.³⁻⁵ If the structure is due to f states, it is surprisingly small and wide since there are 9 f electrons in an atomic-like state. The small magnitude can be accounted for by the fact that the f states are atomic-

¹⁹ S. C. Keeton and T. L. Loucks, Phys. Rev. 168, 672 (1968).

²⁰ A. Y-C. Yu and W. E. Spicer, Phys. Rev. **167**, 674 (1968). ²¹ J. O. Dimmock, A. J. Freeman, and R. E. Watson, in *Proceedings of the International Colloquium on the Optical Properties* and *Electronic Structure of Metals and Alloys* (North-Holland Publishing Co., Amsterdam, 1966), p. 237.

like and transitions to the predominately p- and s-like states above the vacuum level would be weak. The width could be accounted for by electronic-relaxation and lifetime-broadening effects. These points are discussed in the Gd study.³⁻⁵ The rare-earth-band calculations have not been extended to a determination of the f-electron energy levels.^{19,21} It is pointed out that this peak in Dy occurs at a slightly lower energy than the peak in Gd as would be expected of f states.

Secondly, the possibility that the low-energy peak is due to the effects of collective oscillations cannot be ruled out. Several models involving collective oscillations have been proposed to explain certain features observed in photoemission. For example, (1) the excited electrons can be preferentially scattered to lower final states by a collective oscillation $mode^{1,22}$ or (2) a oneelectron excitation and collective oscillation excitation can take place simultaneously.^{23,24} These models and the present photoemission data would predict a collective oscillation mode with an energy between 6 and 6.5 eV.

A third possibility is that the peak is associated with contamination states. This point is discussed in Sec. V C. It is considered unlikely.

C. Structure Produced by Aging

A well-defined peak is observed in the EDC's obtained from the aged samples (see Fig. 6). The peak occurs at $(E-h\nu)+\phi+2.7\pm0.1$ eV, thus it has $(E-h\nu)$ dependence. The observation that the peak grows with time indicates it is associated with foreign atoms collecting at the surface. The phrase "at the surface" is used because it is not known whether the foreign atoms stay on the surface or migrate into the metal. The enhanced number of secondary electrons observed in the aged EDC's is caused by the additional scattering due to the contamination. Data obtained from the sample Bstudied in a tipped-off glass vacuum tube show a broad shoulder at the energy position of the aging peak. The latter observation supports the above interpretation since the character of the residual gas in a tipped-off glass envelope is different from that in an all-metal chamber being pumped continuously. The $(E-h\nu)$ dependence of the aging peak indicates that the structure is associated with the initial state of the optical excitation, see Eq. (1). A reasonable explanation is that these states result from the contamination at the surface.

The probability that the aging peak is produced by contamination at the surface raises the possibility that the peak discussed above, in Sec. V B, is also due to emission from the contamination. This is not considered to be a likely interpretation because the peak at $(E-h\nu)+\phi=6.3$ eV is always observed in the data, and the aging peak is not.

D. Temperature Dependence

The photoemission data show no significant temperature dependence, see Sec. III E. Two conclusions are obtained from these observations. First, the optical transitions are not phonon assisted, which distinguishes the nondirect transition from the indirect transition. In a previous study on Cr, the same temperature result was obtained and discussed.² The discussion is not repeated here.

Second, any changes in the density of states resulting from magnetic ordering are too small to be observed in this experiment. The upper limit placed on the shift in the valence-band ODS is about 0.3 eV. Photoemission measurements in the paramagnetic state and in the magnetically ordered state have also been made on Gd and Cr.²⁻⁴ These experiments also give null results.

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APPENDIX

The purpose here is to consider a model which may be useful in analyzing photoemission data which exhibit scattering by sample contamination. The sample contamination is caused by the residual gases in the vacuum chamber. The model is used to estimate the distribution of emitted electrons which are inelastically scattered (secondaries). The distribution of secondaries is useful for investigating the relative magnitude of structures observed in the ODS.

The photoexcited electrons in the photoemission process migrate to the surface and escape into the vacuum. The model considers the scattering mechanism that the excited electron encounters at the contaminated surface. The contamination may either be on the surface or within a thin region at the surface. The following restrictions are placed on the model: (1) The photoexcitation takes place beneath the contaminated region, and all the photoexcited electrons encounter the same spacial distribution of scattering centers. (2) The electron-electron scattering is only dependent on the electron density of states D(E) that results from the contamination, that is, the matrix elements for the scattering process are independent of energy. (3) D(E)is a constant. (4) Only the emission of once-scattered electrons is considered. Impurity-ion scattering, which is essentially elastic, would be expected to increase the path length of the excited electron in the contaminated region. Because of the increased path length, the probability for inelastic electron-electron scattering is en-

 ²² R. C. Vehse, J. L. Stanford, and E. T. Arakawa, Phys. Rev. Letters 19, 1041 (1967).
 ²³ R. K. Nesbet and P. M. Grant, Phys. Rev. Letters 19, 222 (1977).

 <sup>(1967).
 &</sup>lt;sup>24</sup> R. J. Esposito, L. Muldawer, and P. E. Bloomfield, Phys. Rev. 168, 744 (1968).



FIG. 11. The energy distribution of photoemitted electrons from Dy and the computed distribution of secondary electrons for $h\nu = 11.5$ eV.

hanced. Thus the contaminated region can produce considerable inelastic scattering events even t ough the region must be small for the bulk properties of the sample to dominate the photoelectric process.

The above model is used to derive an expression for the distribution of once-scattered electrons which are emitted. The derivation is similar to that used by Berglund and Spicer for studying intrinsic scattering effects.¹¹ By condition (2) of the model, the probability of a primary electron at energy E' producing a scattered electron at E is given by

$$p(E',E) \propto \int_{E_{F}-(E'-E)}^{E_{F}} dE_{0}D(E)D(E_{0})D(E_{0}+E'-E), \quad (2)$$

where E_0 is the initial energy of the electron that caused the scattering event and $(E_0+E'-E)$ is its final energy. E_F is the Fermi energy. The function P(E') is defined by

$$P(E') = \int_{\boldsymbol{E}_{\boldsymbol{F}}}^{E'} p(E', E) dE.$$
(3)

The fraction of primary electrons at E' producing a once-scattered electron at E is given by 2p(E',E)/P(E'). The factor 2 accounts for the fact that either the electron initially at E' or E_0 can be scattered in the state E. The distribution of once-scattered secondaries is given by

$$S_{I}(E-E_{F}) = A T(E-E_{F}) \\ \times \int_{E_{F}}^{E_{F}+h\nu} N_{0}(E',h\nu) \frac{2p(E',E)}{P(E')} dE', \quad (4)$$

where the factor A contains the parameters which account for the spatial distribution of the scattering centers and the attenuation length for the excited electrons. Condition (1) of the model makes A constant. T(E) is the escape function, and it is zero for $E - E_F < \phi$. The term $N_0(E',h\nu)$ is the number of photoexcited electrons at E' and for the nondirect-transition model with constant matrix elements it is given by the product of the final density of states at E' and the initial density of states at $E' - h\nu$. Taking D(E) to be a constant [condition (3) of the model] and performing the integrations, the final result for the distribution of secondaries is

$$S_{I}(E-E_{F}) = BT(E-E_{F}) \times \int_{E_{F}}^{E_{F}+h\nu} N_{c}(E')N_{\nu}(E'-h\nu) \frac{(E'-E)}{(E'-E_{F})^{2}} dE', \quad (5)$$

where B contains all the constant factors.

The distribution of once-scattered electrons for $h\nu$ =11.5 eV calculated with Eq. (5) is shown in Fig. 11. In Fig. 11, E is the kinetic energy of the electron in the vacuum. The integration was carried out by fitting N_v with a rectangle and a triangle and N_c is a constant. Since B is undetermined, the amplitude of S_I was arbitrarily set. The assumption of a uniform D(E) for large photon energies extends D(E) to unreasonably low energies. Because of the primitive nature of the scattering calculation, no cutoffs for D(E) were tested.

The distribution of once-scattered electrons obtained by this model is similar in character to the distribution obtained for intrinsic scattering. The similarity can be seen by comparing, either the equation used or the calculated curve to those obtained for intrinsic scattering.¹¹ Thus, if a fraction of the electrons attributed to impurity scattering here were due to intrinsic scattering, the nature of the correction would be very similar to the one presently obtained. Although the model is primitive, it is sufficient to demonstrate the effects of secondary electrons in the measured EDC's.

Another mechanism which may account for enhancement of secondary emission by surface contamination is an increase in elastic scattering, where the elastic scattering has been enhanced because the contamination alters the crystal potential at the surface. Thus the path length of the excited electron in the bulk is longer and the number of intrinsic-inelastic scattering events is greater. This mechanism has been discussed by Shay in connection with photoemission studies on lowvacuum cleaved CdSe.²⁵ As pointed out above, the distribution of secondaries obtained from the model presented here are similar to those obtained for intrinsic scattering. Thus, it is difficult to differentiate between the latter mechanism and the model presented here by examining the data.

²⁵ J. L. Shay, Ph.D. thesis, Stanford University, 1966 (un-published).