

# PHYSICAL REVIEW B

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### Densities of Unfilled One-Electron Levels in the Elements Vanadium and Iron through Zinc by Means of X-Ray Continuum Isochromats

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X-ray continuum isochromats have been obtained at a photon energy of 530 eV from bulk samples of vanadium, iron, cobalt, nickel, copper, and zinc under ultrahigh-vacuum conditions. The isochromats have been partially corrected for the smearing due to the spectral window of the two-crystal potassium acid phthalate (KAP) monochromator used and for the distortion due to the nonsingular nature of the electron spectra in the samples. The corrected data may be interpreted as measures of the densities of available one-electron states in these materials.

#### INTRODUCTION

Beginning with the work of Ohlin in the early 1940's, x-ray continuum isochromats have been used as a means of obtaining information about the energy densities of unfilled electron states above the Fermi level in metals.<sup>1-13</sup> Isochromats are generally obtained with an x-ray crystal monochromator and a monoenergetic electron beam incident on an x-ray-tube-anode sample. Bombarding electrons make transitions to vacant states near the Fermi level and produce x-ray photons. As the energy of the electron beam is increased, the onset of this continuous x-ray spectrum is displaced toward higher energies so that it moves into and past the monochromator window. The data recorded are x-ray intensity as a function of anode voltage. Figure 1<sup>13</sup> shows the process with transitions corresponding to different portions of an idealized isochromat drawn in. If the probability for an incident electron to stop in the solid with concurrent emission of an x-ray photon is independent of the final-state energy, then the intensity of the isochromat would be proportional to the density of one-electron states above the Fermi level in the anode. Accordingly, x-ray continuum isochromats have been interpreted as approximating

the relative densities of available states in the anodes from which they are made. This amounts to assuming that the matrix elements for the transitions involved in the production of an isochromat are constant over the range of energies observed, and that electron-transport effects can be ignored. Even though the possibility of variations in the matrix element must not be overlooked,<sup>14</sup> it is possible that under certain conditions<sup>15,16</sup> x-ray continuum isochromats are relatively free from these and other effects that generally complicate the interpretation of experiments which yield information about densities of electron states in solids. For instance, x-ray-photon-absorption studies give information about the density of available states above the Fermi level, but the results are influenced by the presence of an inner-shell vacancy, the width of the inner level involved, bound states, selection rules, and scattering interferences. Some of these effects can be seen clearly in data presented in Ref. 17. Characteristic x-ray-line excitation curves and appearance-potential spectra also contain information about densities of available states; but here a different problem is encountered, since by these methods one expects to obtain information related to the density of available two-electron states or to a self-convolution of the density of

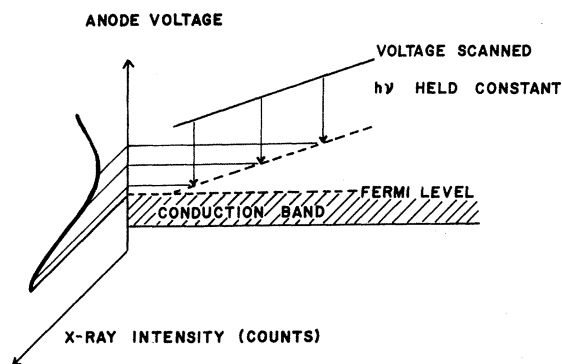


FIG. 1. X-ray continuum isochromat and associated energy-level diagram (schematic). Transitions contributing to the x-ray intensity for different anode voltages are shown (Ref. 13).

states. A discussion of these methods is given in Ref. 18. Ultraviolet-photoemission experiments also reveal information about the densities of available one-electron levels in solids, but here the density of occupied levels is also involved, so that what is measured is a joint density of states.<sup>19-21</sup> Ion-neutralization spectroscopy provides information about the energy distribution of filled electron states.<sup>22</sup> This method appears to be better suited to studying the surface structure of solids than to determining their bulk characteristics. The isochromat method used in the present work may also be open to the same objection, since electron-diffraction studies indicate that electrons with several-hundred-volts kinetic energy can only penetrate through at most the first few atomic layers at the surface of a solid.<sup>23</sup>

When these methods are compared, they often give similar results for the same material, so that certain features can be consistently associated with corresponding structures in the electronic structure of the substance being studied. The remaining differences are caused by a variety of effects including transport phenomena and varying transition probabilities, and these must be accounted for before definitive comparison between band-theoretical calculations and experiment can be possible.<sup>18</sup> In the present work the problem of bombarding electron transport in x-ray tube anodes is treated in a new way, which will be described. The problem with transition probabilities remains, but is probably minimal within bands of states characterized by a single orbital symmetry. To the authors' knowledge, no theoretical calculations of x-ray continuum isochromats (as opposed to densities of states) have been attempted, although the recent work of McCaffrey, Nagel, and Papaconstantopoulos on the nickel *L*-x-ray absorption edges suggests that this should now be possible.<sup>18</sup>

Several experimental difficulties need to be over-

come if x-ray continuum isochromats are to be used to maximum advantage as a source of information about densities of vacant electron states in solids.

(i) An x-ray monochromator with a high transmission is needed, since x-ray intensity is low at the onset of the continuum. The instrument must also have a high resolving power. In this work these requirements were met with a two-crystal vacuum monochromator using potassium acid phthalate (KAP) crystals. A linelike enhancement in the x-ray reflectivity of KAP at 530 eV made possible photon counting rates some 20 or more times greater than could have been obtained at nearby energy settings.<sup>24</sup> Since a two-crystal instrument was used, it was possible to obtain an estimate of the monochromator window function and to unfold it later from the recorded isochromats.

(ii) The form of the bombarding-electron spectrum in an x-ray-tube anode must be taken into account. If extremely thin anodes (foils on the order of tens of angstroms thick) could be used, this spectrum would maintain its initial near- $\delta$ -function form and the problem would not arise. However, sufficiently thin foils cannot stand the intense electron bombardment involved, and, even if they could, their use would further diminish the already low counting rates characteristic of this type of experiment. A realistic alternative involves unfolding an estimate of the energy spectrum of the electrons in the x-ray-tube anode from an isochromat, and this was the method adopted here. A thick-target isochromat is thought of as representing the fold of an ideal thin-target isochromat with an effective electron energy spectrum which takes into account the way in which initially monoenergetic electrons lose energy as they penetrate the surface layers of a thick anode. If an estimate of this electron spectrum can be obtained, it can be unfolded from the isochromat to obtain a curve which is better suited to comparison with density-of-states calculations and other experiments than the original isochromat itself. In this work photoelectron-emission spectra from bulk samples of the elements studied were used for the estimates needed to correct the x-ray continuum isochromats. Monochromatic x-rays were used to excite photoemission, and the profiles of characteristic photoemission peaks with energies as near as possible to 530 eV supplied the necessary electron spectra. The justification for this choice of electron spectrum rests on the observation that in both photoemission spectra and x-ray continuum isochromats one deals with the superposition of initially monoenergetic fluxes of electrons that have penetrated successively greater thicknesses of material. This argument is developed at greater length in Appendix A. Other workers have used a different

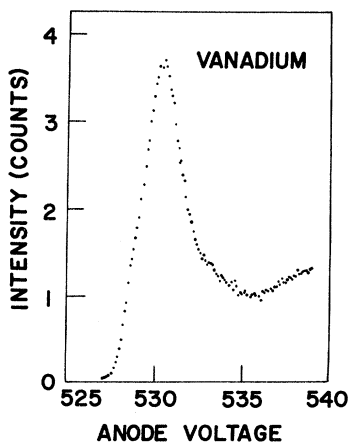


FIG. 2. X-ray continuum isochromat for vanadium.  
 $h\nu = 530$  eV.

model for the electron spectrum in an anode.<sup>5,11,16</sup> Electron-backscattering experiments suggested that there might be a region near the onset of an isochromat where the effect of electron inelastic scattering was minimal, so that in this region an isochromat could be compared directly with the corresponding density of states in the solid. The present work is an attempt to improve on this earlier approach.

The electron-emission spectra used were obtained by one of the authors in the laboratory of Dr. Henke at the University of Hawaii and from Ref. 25. Good agreement between spectra from these two sources was found in the cases where comparison was possible. The technique used at the University of Hawaii is described briefly in Appendix B.

#### ISOCROMATS

The isochromats presented here were obtained with a two-crystal vacuum x-ray monochromator set to pass 530-eV ( $\lambda = 23.2$  Å) photons. Working at this energy setting has a double advantage: first, it permits making use of the peak in the x-ray reflectivity of KAP at this energy.<sup>24</sup> Second, the effect of electron energy smearing is reduced, relative to what would occur at higher photon energies, since the ratio of elastic to inelastic electron scattering is apparently more favorable at lower energies.<sup>6,16,26</sup> Photon detection was by means of a flowing-gas proportional counter. The typically  $2 \times 10^{-9}$ -Torr vacuum in the x-ray tube was separated from the  $10^{-3}$ -Torr vacuum in the monochromator by a Formvar window, and a similar thin film of Formvar supported on a nylon mesh served as a window for the proportional counter. Together these windows had a transmission of about 50%. The anodes were prepared from high-purity sheet-

metal stock, except for the zinc anode, which had to be water cooled on account of this metal's higher vapor pressure. Electropolishing was employed for the final surface finish of the anodes, and the x-ray tube was backfilled with dry nitrogen to minimize anode-surface oxidation during pumpdown. Thoria-coated iridium filaments were used for the electron source, which could supply 50 mA without significantly contaminating the anodes, that is, without causing the isochromats to change with time. These filaments were heated by a half-wave rectified 60-Hz current, and a gating circuit was provided for counting only while the voltage drop across the filaments was zero.<sup>5</sup> A voltage divider, potentiometer, and standard cell were used to monitor the anode voltage, which was generally kept constant to within  $\pm 5$  mV for any one data point.

The uncorrected continuum isochromat obtained for vanadium is shown in Fig. 2 and those for iron, cobalt, nickel, copper, and zinc in Fig. 3. No backgrounds have been subtracted.

Spectrum scans of the oxygen  $K_{\alpha}$  line at 525 eV were made using the monochromator in the spectrometer mode and served to monitor anode-surface-oxide contamination. As part of this work attempts were made to take isochromats of chromium and manganese electrolytically deposited on copper. The isochromats obtained cannot be considered typical of these metals in their unoxidized state and are consequently not reproduced here, but the results are of interest because oxygen  $K_{\alpha}$  line scans corresponding to states of relatively severe surface oxide contamination were taken from these anodes. Figure 4 shows oxygen  $K_{\alpha}$  region spectra obtained with a bombarding electron energy of 2 keV from the chromium and manganese anodes and two others. The curve showing the highest level of oxide contamination was made from the manganese anode. This anode appeared metallic when it was taken from the plating bath but had turned somewhat sooty by the time the x-ray tube had been evacuated. The chromium anode shows the next highest level of oxide contamination. The two lower curves show the range of oxide contamination over which the isochromats in Figs. 2 and 3 were made. In the spectra made in conjunction with the isochromats for iron, cobalt, nickel, and copper, the oxygen  $K_{\alpha}$  line has less than  $\frac{1}{20}$  the amplitude it has in the spectrum made from the unsatisfactory manganese anode. For zinc this ratio is about 1:10. Mossy zinc was melted in air to make the anode, and this may account for the difference. Another factor that may have contributed to the higher oxidation level in the case of zinc was the lower temperature at which this anode was operated. Unlike the other anodes, the zinc anode could not be heated to incandescence in an ultrahigh vacuum to clean its surface. It is also

possible that the electropolishing process left a thin oxide layer on the anode surface. When this anode was freshly prepared, however, photoemission could be observed from it in air with an ultraviolet light and an electroscope. The spectrum

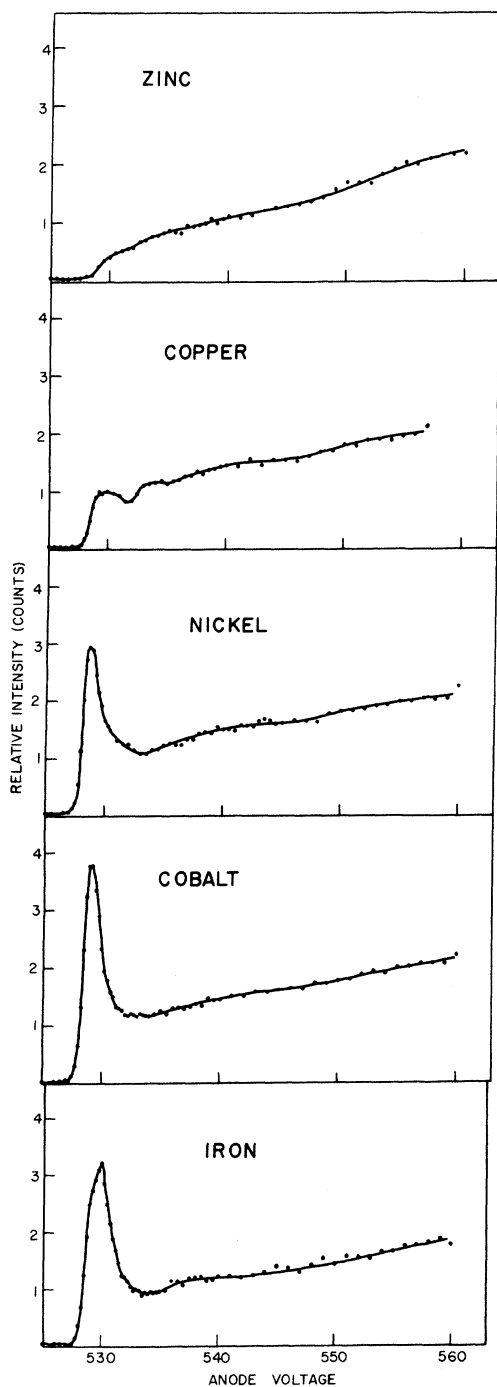


FIG. 3. X-ray continuum isochromats for the elements iron through zinc.  $h\nu = 530$  eV.

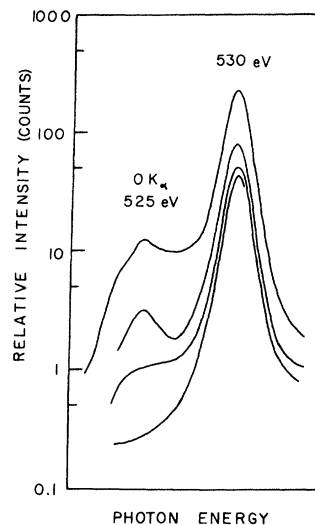


FIG. 4. Oxygen  $K_{\alpha}$  line region spectra made with a two-KAP-crystal spectrometer for a series of anodes. The spectra show the enhancement in the x-ray reflectivity of KAP at 530 eV and different degrees of anode surface oxide contamination.

in Fig. 4 that shows the lowest level of oxide contamination was made from an incandescent cobalt anode.

The most prominent feature in the spectra of Fig. 4 is due to the enhancement in the transmission of the x-ray monochromator at 530 eV. The monochromator was set on this peak to make the isochromats. Each point on one of the curves of Fig. 4 represents the convolution of the monochromator window function with the x-ray spectrum. If there had been no oxide contamination, only continuous x-ray background would have been present, and the incident spectrum would have been nearly constant over the energy range covered. In this limiting case the principal peak in Fig. 4 would represent simply a variation with energy (or crystal dihedral angle) in the area under the monochromator window function. Thus the form of this peak does not convey information about the half-width of the monochromator window function, that is, about the instrument's resolving power. The magnitude of the transmission peak increases with the level of oxide contamination. This is because satellites of the oxygen  $K_{\alpha}$  line extend into the region of the transmission maximum. Thus, one can expect to find a faint excitation curve for a portion of the oxygen  $K_{\alpha}$  line satellite structure superimposed on a continuum isochromat made at a photon energy of 530 eV. However, the form of the excitation curve for this satellite structure is such that an isochromat will only be slightly distorted by this effect.

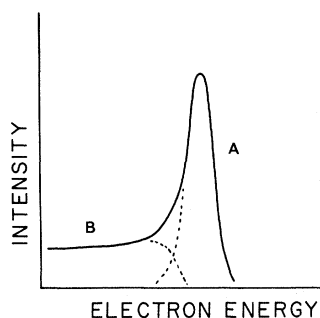


FIG. 5. Characteristic electron emission peak (schematic) showing contributions associated with (A) elastic and (B) inelastic scattering.

#### ISOCHROMAT CORRECTIONS

The first correction made to the x-ray isochromats was for smearing by the spectra window of the two-crystal monochromator. An advantage of the two-crystal x-ray monochromator is that a non-dispersive, parallel-position rocking curve can be used to obtain an estimate of its window function. Since the diffraction properties of KAP crystals vary greatly in the vicinity of 530 eV, it was necessary to use a rocking curve made under special conditions for an estimate of the monochromator window function needed to correct the isochromats. In order to obtain a KAP parallel-position rocking curve for x rays of energies closely centered around 530 eV, Kirby<sup>24,27</sup> found it necessary to provide collimating slits placed in front of the first crystal so that only x rays of energies closely centered around 530 eV could be Bragg reflected to the second crystal. Kirby's rocking curve has a half-width of about 0.8 eV. The unfoldings were carried out by means of an iterative technique described by Schnopper.<sup>28,29</sup> For these calculations points were read at 0.1-V intervals from smooth curves drawn through the data points.

The final stage in the data reduction was to remove the effect of the electron energy distributions in the samples from the isochromats. This was done in the same way the effect of smearing by the monochromator window function had been removed from the experimental data, except that here it was necessary to unfold the appropriate electron energy spectra from the curves. As mentioned earlier, photoemission spectra from samples of the elements studied were used for this purpose. The examination of  $L_{III}$ -shell photoemission spectra obtained at the University of Hawaii and taken from Ref. 25 suggests the interpretation shown in Fig. 5 for the contribution made by  $L_{III}$ -shell photoemission to an electron spectrum. The peak represents electrons that escape from the sample

with their initial energy unimpaird; the ledge, those that have lost some of their initial energy before escaping. Structures that may exist between the peak and the onset of the ledge were not resolved in the spectra used in conjunction with this work. Because the ledge is nearly level, one would expect the ratio of the intensity in the ledge to the integrated intensity in the peak to be characteristic of electron inelastic scattering in the sample and not related to the line shape of the exciting radiation, the width of the  $L_{III}$  level, or the width of the electron spectrometer window function. Estimates of the ratios of ledge intensity to integrated peak intensity for corresponding elements using data from Ref. 25 and from the University of Hawaii agreed to within about 20%. For vanadium this ratio was found to be about  $0.08 \text{ eV}^{-1}$ ; for iron, cobalt, and nickel,  $0.07 \text{ eV}^{-1}$  was used.  $0.045 \text{ eV}^{-1}$  was the value obtained for the same quantity for copper and zinc. Before the photoemission spectra were used to correct the isochromats, they were modified slightly, since the effects of the  $L_{III}$  inner level widths, of the aluminum and magnesium  $K_{\alpha}$  linewidths, and of the width of the electron spectrometer window would not have been present in the bombarding electron spectra in the isochromat experiments. Thus the widths of the initial spikes were reduced to 0.1 eV, roughly the value of  $kT$  in the x-ray-tube filaments. The low-energy ledges were chosen to preserve the ratios of ledge intensity to integrated peak intensity given above. The final corrected isochromats are shown in Figs. 6 and 7. That they do not fall to zero precisely at 530 V can be attributed in part to the effect of the work function of the x-ray-tube filaments.<sup>30</sup> These curves are believed to resemble what would be obtained if the ideal thin-foil isochromat experiment mentioned earlier could be performed with these same metals.

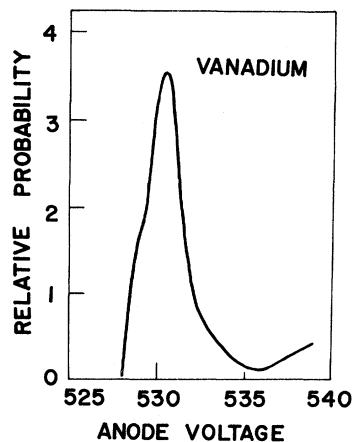


FIG. 6. Relative probability for the production of 530-eV continuous x-ray photons in vanadium.

## DISCUSSION

The corrected isochromats presented here are in good qualitative agreement with other experiments which are sensitive to densities of unfilled

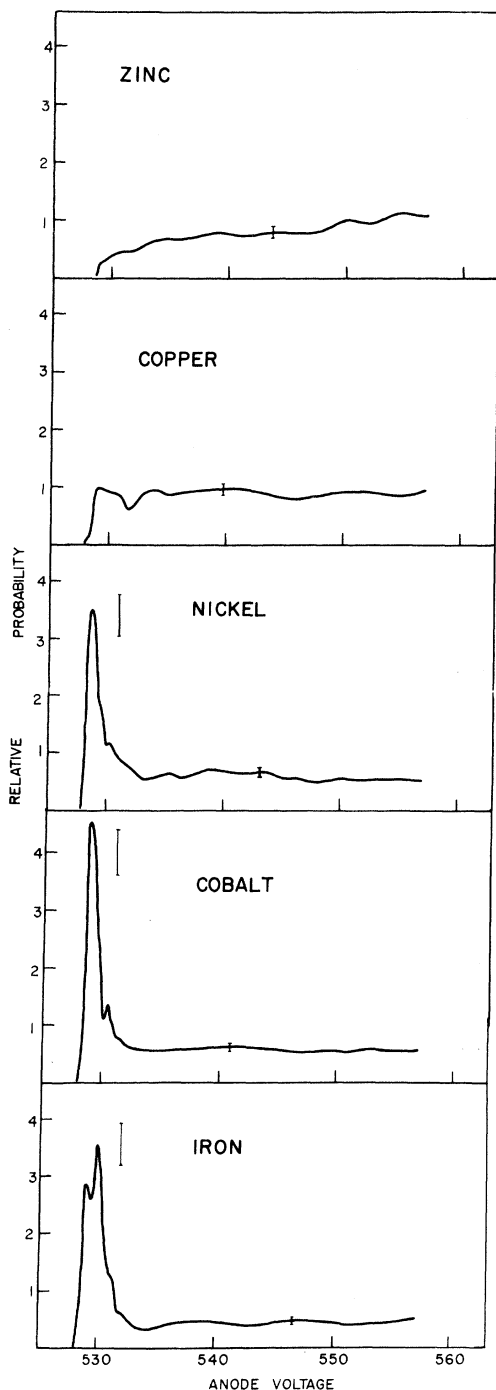


FIG. 7. Relative probabilities for the production of 530-eV continuous x-ray photons in the elements iron through zinc.

states. For example, x-ray absorption spectra for some of these elements<sup>31,32</sup> also indicate a progressive filling (from iron through copper) of a relatively narrow band of states. This same behavior can be seen in characteristic x-ray-line excitation curves<sup>33</sup> and in ultraviolet-photoemission experiments,<sup>21</sup> and is consistent with what has been observed in x-ray photoemission experiments.<sup>34,35</sup> Since factors other than the density of states enter into these experiments in different ways, it is unreasonable to expect complete agreement between them. Perhaps the most serious problem of interpretation inherent in the present method is that different transition probabilities can be expected to apply for states of different orbital symmetry, so that densities of states of different symmetries are weighted differently within each of the experimental curves shown in Figs. 6 and 7. In particular, one might expect the ratio of the heights of the peaks to the "backgrounds" extending toward higher energies in the data for iron, cobalt, and nickel to be thus influenced. Effects of this sort may account for some of the difference between the results for copper here and those obtained by Berglund and Spicer.<sup>19,36</sup>

Resolution in this experiment may be limited by lifetime broadening.<sup>18,19</sup> This is suggested by the gradual character of the initial rise in the corrected isochromats, which is less abrupt than would be the case if the thermal broadening of the onset of vacant states given by the Fermi distribution were the only effect at work. If this is true, then it is an indication that some of the fine structures on the high-energy sides of the initial peaks for iron, cobalt, and nickel (Fig. 7) are probably spurious and only artifacts of the data processing. Also, the broad, low peak at the onset of the curve for copper may be double, in agreement with what has been reported by Berglund and Spicer.<sup>19</sup> The splitting in the initial peak for iron is suggested in the raw data for this element; however, such splitting is not predicted in at least one recent density-of-states calculation for iron.<sup>37</sup> The corrected isochromat for vanadium (Fig. 6) shows some agreement with theoretical density-of-states curves presented in Refs. 37 and 38 if the limited resolution of the experiment is taken into account. This is illustrated in Fig. 8, where the theoretical curve obtained by Papaconstantopoulos, Anderson, and McCaffrey has been smeared with a Gaussian distribution with a half-width of 1 eV to approximate the effect that would be expected if their density of states were viewed by an experimental method having about the same resolution as the one used here. Reference 37 indicates that over the range of energy shown in Fig. 8 the experiment is sampling  $d$  states with little admixture of  $s$  states. Reference 37 also gives calculations for

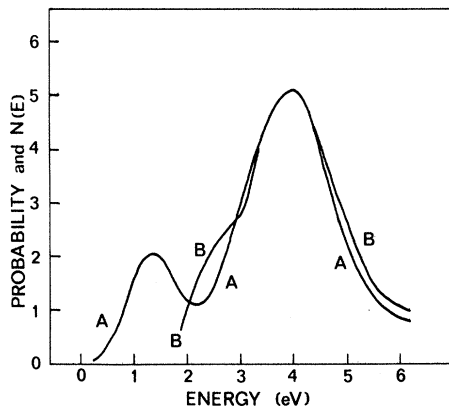


FIG. 8. (A) Theoretical density of states  $N(E)$  for vanadium obtained by Papaconstantopoulos, Anderson, and McCaffrey (Ref. 38). (B) Corrected isochromat for vanadium. The theoretical density of states has been broadened as described in the text. The curves have been adjusted so that the principal peak heights and energies match.

cobalt, nickel, and copper. For these elements the results of comparison appear less conclusive, since the  $d$  band is more nearly filled and narrower than is the case for vanadium.<sup>39</sup> The mixture of cubic and hexagonal phases present in cobalt may add to the problem of interpreting the data for this element.

#### ACKNOWLEDGMENTS

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#### APPENDIX A: CHOICE OF ELECTRON SPECTRUM

When monoenergetic x rays are used to bombard a clean metal sample, relatively sharp photo- and Auger-electron emission peaks are observed in the energy spectrum of the electrons ejected from the sample. The energy of a peak is given by the difference between the binding energy of the appropriate inner level and the energy of the incident x-ray photons (photoemission) or by the difference between characteristic excitation energies (Auger peak). Such a peak will show the effect of inelastic electron scattering in the sample by the presence of a ledge or tail on its low-energy side, as is illustrated in Fig. 9. When made under the appropriate conditions, a photoemission peak and its associated ledge should be similar to the energy spectrum needed to unfold the effect of bombarding electron energy smearing from a thick-target isochromat. Suppose  $F(E, x)dx$  represents

the relative number of photoelectrons escaping from a sample per second with energy  $E$  that were originally excited to a characteristic energy  $E_0$  at a depth  $x$  beneath its surface. Then  $F(E, x)$  should also be roughly proportional to the flux of electrons with energy  $E$  that would be available to produce continuous x-ray photons at the same depth  $x$  beneath the surface of the sample if it were bombarded with monoenergetic electrons of initial energy  $E_0$ , since the electron scattering processes involved would be similar. Suppose continuous x-ray emission from the same sample can be described by a relation of the form

$$I(h\nu, E_0) \propto \int_{x=0}^{\infty} \int_{E=h\nu}^{E_0} N(E-h\nu)F(E, x)dE dx, \quad E_0 \geq h\nu \quad (\text{A1})$$

where  $I(h\nu, E_0)$  is the intensity (counts/sec) of continuous x-ray emission with photon energy  $h\nu$  produced by bombarding the sample with electrons of initial energy  $E_0$ ,  $N(E-h\nu)$  is the density of available states above the Fermi level (which is taken as the zero of energy), and  $F(E, x)$  is proportional to the flux of electrons with energy  $E$  at a depth  $x$  beneath the surface of the sample. Then

$$\int_{x=0}^{\infty} F(E, x)dx \quad (\text{A2})$$

can be unfolded from (A1) to obtain  $N(E_0-h\nu)$ , the desired density-of-states curve. But from the first part of the argument it follows that (A2) is also proportional to the total photoemission at energy  $E$  from the sample, a quantity which can be measured. Since the form of a photoemission peak

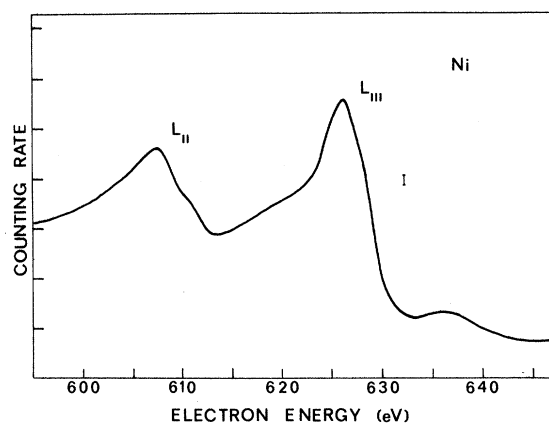


FIG. 9. Energy spectrum of  $L_{II}$ - and  $L_{III}$ -shell electrons ejected from bulk nickel by aluminum  $K_{\alpha}$  radiation. The zero of counting rate has been suppressed. The small peak on the high-energy side of the  $L_{III}$  photoemission peak is caused by the aluminum  $K_{\alpha 3\alpha 4}$  x-ray satellite line in the aluminum radiation used to excite emission. The corresponding structure for the  $L_{II}$  peak is present, but not so clearly resolved (Ref. 25). These structures are not of interest in the present work.

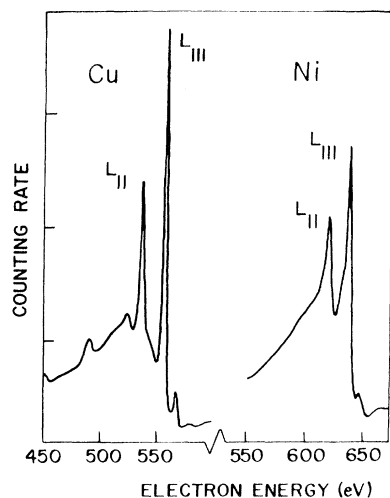


FIG. 10. Energy spectra of  $L_{II}$ - and  $L_{III}$ -shell electrons ejected from copper and nickel by aluminum  $K_{\alpha}$  radiation. The zeros of counting rate have been suppressed.

is not strongly dependent on the photon energy at which it is made, only one photoemission spectrum is needed for each element studied. Since the object of the photoemission experiment is to produce photoelectrons of initial energy roughly equal to the photon energy at which the x-ray continuum isochromat is made, the photons used to excite photoemission should be of greater energy than those studied in the isochromat experiment. As previously mentioned, this difference should be of sufficient magnitude to make up for the binding energy of the level from which photoelectrons are ejected.

It is important to point out the approximations

inherent in the above analysis. First, a factor taking into account x-ray absorption in the sample was omitted from inside the integral in (A1) since at comparable energies electrons are less penetrating than x rays. The argument as presented is essentially one-dimensional in character and does not take into account properly the fact that electrons are scattered in all directions as they penetrate a solid. It is difficult to assess the effect of this on the results obtained. Finally, omitting the transition probability from inside the integral in (A1) constitutes an additional approximation which has already been mentioned.

#### APPENDIX B: PHOTOEMISSION SPECTRA

Some of the photoemission spectra required for this work were made in the laboratory of Dr. Henke at the University of Hawaii. Samples of iron, cobalt, nickel, copper, and zinc were bombarded by magnesium or aluminum  $K_{\alpha}$  x rays, and the electrons ejected were energy analyzed. Nitrogen-ion bombardment was used for cleaning the samples before spectra were taken. In each case aluminum or magnesium excitation was chosen to obtain  $L_{III}$ -shell photoemission with an energy as near as possible to 530 eV. The hemispherical electrostatic spectrometer used a filtered x-ray source operating in the same vacuum chamber and a Cu-Be electron multiplier for electron detection. Spectra were made at pressures in the  $10^{-7}$ -Torr range. Typical photoemission spectra are shown in Fig. 10. The best results were achieved with nickel, copper, and zinc. The spectra from cobalt were slightly less distinct than those from the first three elements, while the iron spectra showed signs of surface contamination. Additional information on the instrumentation employed can be found in Ref. 40.

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## Influence of Grain Boundaries and Lattice Defects on the Optical Properties of Some Metals

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A simple theory is developed to study the influence of grain boundaries and lattice defects on the optical properties of metals. It is shown that even for well-annealed thin-film samples the influence of grain boundaries on the optical properties is not negligible when the reflectivity is high. The model is used to show that the anomalous absorptivity in alkali-metal films evaporated onto cold substrates recently reported by Palmer and Schnatterly is due predominantly to a plasma resonance in the grain boundaries. It is also found that the non-Drude behavior of Ag in the visible and the supplementary absorption in poorly crystallized Au films, observed by Devant and Theye, most probably is due to such plasma resonances in the grain boundaries.

### I. INTRODUCTION

Optical measurements have been used extensively as a tool for investigating the electronic structure of matter for many decades—and the interest in such measurements has been particularly strong in recent years. These measurements have been helpful in establishing values of parameters used in band-structure calculations.

The optical properties are often sensitive to the sample structure. Two types of samples are used in optical measurements: bulk crystals (often single crystals) and evaporated films. The former, prepared by mechanical- and electrical-polishing techniques, will always have scratches, bumps, and pits in the surface and these will influence the measurements. These types of sample imperfections have been studied extensively over the last few

years. Thin evaporated films consist of small crystallites of diameter generally less than  $1 \mu$ . These crystallites are often randomly oriented; there are dislocations, lattice vacancies, and other defects along the grain boundaries. Little has been done to study the influence of the crystallite structure on the optical properties but, as shown by Devant and Theye,<sup>1</sup> the optical properties may depend dramatically upon the sample structure.

In this paper the influence of grain boundaries on the optical properties of some metals is examined using a simple model. In Sec. II the model is outlined and in Sec. III a simple theory is presented. In Sec. IV the general effects caused by grain boundaries and sample imperfections for the metals K, Ag, and Au are discussed. An attempt is made to estimate the minimum grain size necessary to give essentially bulk conditions. What effects