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Soft-X-Ray $L_{2,3}$ Spectrum and Electronic Band Structure of Chromium

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The soft-x-ray $L_{2,3}$ emission and absorption spectra from pure chromium are shown and the effects of satellite emission and self-absorption are assessed. Features of the L_3 spectrum are discussed in terms of the energy-band structure. Results are evaluated by comparing the L_3 spectrum with the x-ray K and M spectra, with ultraviolet photoemission measurements, and with band-structure calculations. There is good agreement between theory and experiment as to the width of the occupied states, the position of the Fermi energy, and the position of most maxima and minima in both the occupied and vacant portions of the density of states. Some disparities are also observed but they involve primarily the fine features of the structure.

I. INTRODUCTION

The use of soft-x-ray spectra (SXS) for studying the band structure of 3*d* transition metals has been discussed in many publications over the last 35 years or so. Until quite recently, in fact, SXS was the only readily available experimental method of probing the structure as far as 5–10 eV below the Fermi energy (E_F). The last several years, however, have witnessed the growth and development of some new deep-band techniques such as ultraviolet photoemission spectroscopy[1] (UPS), ion-neutralization spectroscopy[2] (INS), and x-ray photoemission spectroscopy[3] (XPS). Each of these techniques has certain advantages in specialized cases, and each is capable of providing information related to the density of states of the material being studied. *None* of them, however, gives a direct picture of the density of states. Although these techniques all involve different types of electronic transitions and transtion probabilities, it can be quite instructive to compare the SXS, UPS, INS, and XPS results with each other and with theoretical calculations as has been done for Ni and Cu.[4,5] One can realistically expect to obtain reasonably good agreements as to the position of the Fermi energy, the width of the occupied states, and the position of the main maxima in each of the curves. Such agreements can lend confidence to both the experimental techniques and the theoretical computations of the band structure.

To date, the bulk of experimental and theoretical work performed on the 3*d* metals has been concentrated on the heavier members of the series: Fe, Co, Ni, and Cu. Little has been done on the lighter elements Ti, V, and Cr. This author has previously published the SXS $L_{2,3}$ spectra of Ti[6] and V[7] and Eastman has shown their UPS curves.[8] So far, however, no INS or XPS data has appeared for these elements. The purpose of this paper is to show recently obtained SXS data for Cr and relate them to the SXS results for Ti and V, to the UPS results, and to the available theoretical calculations. Points of agreement and disagreement in the comparisons will be discussed.

Of all of the deep-band experimental techniques mentioned above, SXS can supply more total information about the band structures of the transition metals than any one of the other techniques. Not only can one obtain data about the occupied band states by using emission spectra, but valuable information about the unoccupied states can be found in the absorption spectra. The other techniques (UPS, INS, and XPS) do not readily yield data on the normally unoccupied states. Furthermore, the x-ray results are capable of differentiating between the various wave symmetries admixed into the valence/conduction band. The K spectrum, for instance, reflects only the distribution of p symmetry in the band, while the $L_{2,3}$ and $M_{2,3}$ spectra reflect the distribution of s and d symmetry.

It is the s and d states which are of primary interest in the transition metals. For the 3*d* series elements, the commonly accepted picture of the energy-band structure is one of a narrow 3*d* band of high-level density overlapped by a broad 4*s*-4*p* band of low-level density. The 3*d* states are primarily responsible for the majority of transition-metal characteristics such as the electrical and magnetic properties. In SXS one is therefore interested in studying those parts of the spectra which are due to transitions involving the *s* and *d* states. For the 3*d* transition series, this can be done with either the $L_{2,3}$ or $M_{2,3}$ band spectra. From experimental considerations, we find the $L_{2,3}$ spectra much easier to obtain. The L_3 band represents the transition $3d4s \rightarrow 2p^{3/2}$ and the L_2 band, the transition $3d4s \rightarrow 2p^{1/2}$.

As is well known, the intensity distribution of an x-ray valence-emission band as well as the variation in the absorption coefficient μ is related to the density of states times the transition probability and so does not give a direct picture of the density of states. Nevertheless certain features of the density of states such as the position of the Fermi energy, the total width of occupied states, and energy positions of maxima and minima in both occupied and vacant states can be reliably determined from good x-ray data. It is this use of SXS results which are of primary interest in this report on chromium.

II. EXPERIMENTAL TECHNIQUES

A. Instrumentation

The plane single-crystal vacuum spectrometer used to obtain the SXS spectra is the same as described previously.[6,7] Characteristic x-ray spectra are produced by direct electron-beam bombardment of the target material. The anode assembly is constructed so that the x-ray takeoff angle is continuously variable between 0° and 90°. A flow proportional detector with a Formvar window and argon-methane flow gas is used at a reduced pressure of 120 Torr. The spectrometer vacuum under normal operating conditions is about 1×10^{-6} Torr.

A rubidium acid phthalate crystal (RAP, $2d = 26.118$ Å) was used in obtaining the Cr $L_{2,3}$ spectra. These spectra were recorded in two ways; by tracing out directly on a strip-chart recorder and by a step-scanning procedure in which accumulated data (emission intensity vs 2θ angle) were printed out on a Teletype tape. Wavelength positions of the spectral features measured in this manner have a probable error of ± 0.02 Å (± 0.3 eV) and wavelength differences could be measured to ± 0.005 Å (± 0.1 eV). The data points on the spectral curves have a statistical deviation of 2–3% at the peak maxima and less than 1% at the tails.

The effective diffraction pattern of the spectrometer (window width) was determined to be 0.81 eV at full width at half-maximum (FWHM) at the Cr L_3 band maximum (21.7 Å). However, because the window width varies with the wavelength (i.e., 2θ angle) and the exact shape of the window is not shown, the Cr band spectra shown in this report have not been corrected for instrumental broadening. This is not considered to have any significant effect on the conclusions reached concerning the spectra. An instrumental correction will not change the position of the emission and absorption features and would have negligible effect on the total bandwidth.

For absorption studies the continuum from a platinum target was used. A special sample wheel held the absorption-film specimens and was placed between the dispersing crystal and the detector. This wheel could be moved into or out of position from outside the vacuum without disturbing any of the operating conditions.

B. Sample Preparation

The chromium metal used for both the emission and absorption studies was of 99.9+-at.% purity. Target specimens used to obtain the emission spectra were prepared by two methods. The first method consisted of vacuum evaporating a thin film of chromium directly on the anode assembly. The other method was to melt the chromium into a solid chunk about $\frac{1}{8}$ in. thick, $\frac{1}{2}$ in. wide, and 1 in. long. This chunk was then mechanically ground and polished to a smooth mirrorlike finish and mounted on the anode assembly. Both types of sample yielded exactly the same $L_{2,3}$ spectrum under comparable excitation conditions.

Absorption specimens were prepared by vacuum coating a layer of chromium on a Formvar substrate of about 6000-Å thickness. Seven specimens were made with the chromium thickness varying from about 0.10 to 0.35 mg/cm². The optimum thickness for obtaining good spectra appeared to be about 0.20 mg/cm².

III. RESULTS AND DISCUSSION

The chromium $L_{2,3}$ emission and absorption spectrum from the pure metal is shown in Fig. 1(a). Emission components are labeled with capital letters, absorption components with lower-case letters. The energy position of each of these components is listed in Table I. There is general agreement between the emission spectrum shown here and that shown by previous workers.[9–13] Bonnelle[10] has also shown the Cr L_3 absorption spectrum but apparently with insufficient resolution to see the fine structure adjacent to the L_3 edge as found by the present author.

As was previously noted for Ti and V,[6,7] the Cr L_3 emission band can be seriously distorted by

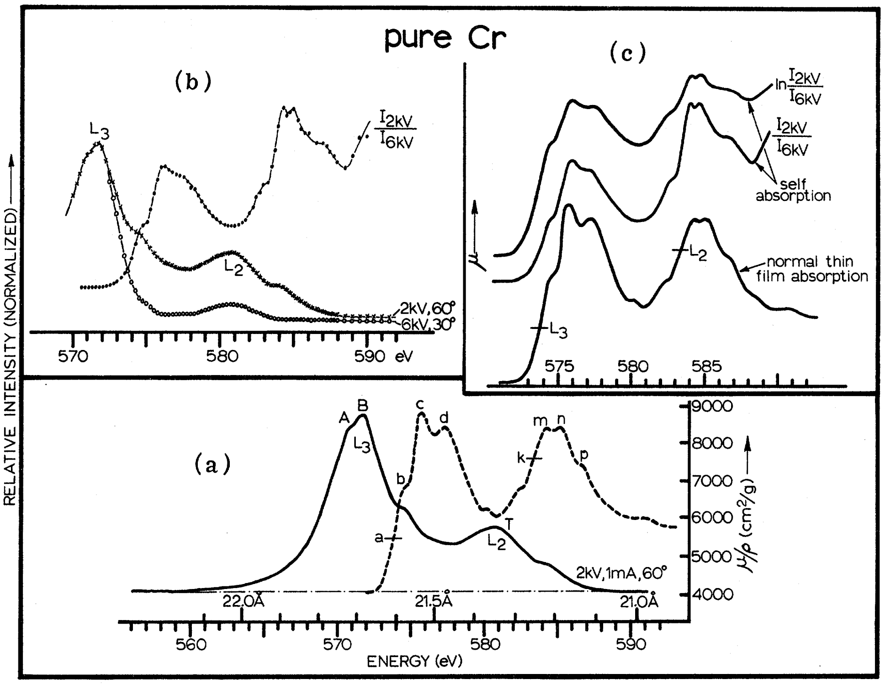

FIG. 1. (a) Uncorrected Cr $L_{2,3}$ emission (solid line) and absorption (dashed line) band spectra from pure metal. Peak heights normalized. (b) Method of obtaining self-absorption spectrum of Cr. (c) Comparison of self-absorption spectra with normal thin-film photon absorption spectrum. Peak heights normalized.

self-absorption effects. As the potential of the bombarding electron beam is increased and/or the takeoff angle decreased, there is a severe intensity loss of the high-energy side of the L_3 maximum as seen in Fig. 1(b). The numbers at the lower-right spectral tails indicate the beam voltage and takeoff angles used to obtain the spectra. Also notice from the two emission spectra of Fig. 1(b) that the intensity of the L_2 peak maximum greatly decreases with respect to the L_3 peak maximum as the beam penetration increases. This is precisely the same effect observed previously for the Ti and V spectra[6,7] and is caused primarily by the $L_3 \rightarrow L_2$ Auger transition. The L_2/L_3 intensity ratio for Cr varies with beam voltage and takeoff angle in the same manner shown previously for Ti.[6]

The $L_3 \rightarrow L_2$ Auger effect places the atom in a doubly excited state and any L_3 band emission which occurs subsequent to this state will fall at slightly higher energy than the normal single-vacancy emission. These higher-energy emissions are the well-known band "satellites" which can be quite strong in the transition-metal $L_{2,3}$ spectra and are the major reason why the self-absorption effect is so noticeable in these elements and their compounds.

The very fact that self-absorption cuts off part of the L_3 emission structure as seen in Fig. 1(b) indicates that the L_3 absorption edge overlaps part of the L_3 emission band. That part of the band which is overlapped is assumed to be satellite structure and it appears to reach maximum intensity at a beam energy of two to three times the L_3 threshold voltage. Therefore, as the voltage of the bombarding electron beam is increased from threshold on up, the satellite emission is growing but is at the same time being suppressed by the self-absorption effect. There is little wonder then that much disagreement is to be found in the literature on the band shapes obtained by different investigators using different experimental conditions.

Obviously, if one expects to use an L_3 emission band to provide information about the band structure, especially in the vicinity of the Fermi energy, both satellite emission and self-absorption effects must be removed from the spectrum. Self-absorption can usually be made negligible by the proper combination of excitation voltage and takeoff angle but satellite emission will be present at any beam

TABLE I. Energy positions of intensity maxima in Cr $L_{2,3}$ emission and absorption spectrum from pure metal.

Peak	eV		Å (± 0.01)
A	570.9 ± 0.2		21.72
B	571.6 ± 0.2		21.69
T	580.8 ± 0.3		21.35
a (L_3 edge)	573.8 ± 0.1		21.61
b	574.6	± 0.2	21.58
c	575.7		21.54
d	577.2		21.48
k (L_2 edge)	583.3		21.26
m	584.2		21.22
n	585.2		21.19
p	586.7		21.13

voltage higher than L_2 threshold. Liefeld[14] and Hanzely[15] have shown that at electron-beam voltages less than L_2 threshold but greater than L_3 threshold, the satellite emission is no longer present for the L_3 bands of Cu, Ni, Co, and Fe. Obtaining an L_3 band profile at threshold excitation is quite difficult, however, and the author has been unable to do it for Ti, V, or Cr because of insufficient emission intensity. The correct band shape can nevertheless be reasonably well determined by assessing the effects of self-absorption and by knowing the position and form of the absorption edge. Such an approach is used here for the L_3 band of Cr which will be discussed a little later in relation to the band structure.

Although self-absorption can indeed be a problem at times, it can also be a very helpful phenomenon in determining certain features of the absorption spectrum. This is especially true for many transition-metal compounds for which adequate absorption films are extremely difficult to make. The procedure for obtaining self-absorption spectra is demonstrated in Fig. 1(b). Two emission spectra are used; one afflicted with little or no self-absorption and the other afflicted with a very large amount of self-absorption. One then measures the point-by-point intensity ratio of the two spectra and plots these ratios as a function of the photon energy to obtain the results shown in Fig. 1(b). Such a self-absorption spectrum is very similar in appearance to the normal thin-film photon absorption spectrum although they are not strictly equivalent. This self-absorption technique was first demonstrated by Liefeld[16] for heavier $3d$ elements and was put to practical use by the present author for determining the structure of some compounds of Ti, V, and Cr.[6,7,17–19] An additional advantage of the technique is that both emission and absorption spectra can be obtained from the same sample at the same time so that they are automatically matched properly on the energy scale and represent the same physical and chemical state of the material.

A comparison of the L_3 self-absorption and thin-film photon absorption spectra for Cr is shown in Fig. 1(c). The self-absorption spectra are plotted in two ways: as the directly determined emission intensity ratio and as the log of this ratio. For normal absorption studies, the common practice is to use the log function but for self-absorption spectra it is often found that the straight ratio itself gives a better approximation to the true photon absorption than does the log of the ratio.[14–19] The important part of the comparison of Fig. 1(c) is that the main features of the two types of spectra agree quite well. The absorption edge, the maxima, and the minima are all reproduced at the same energy positions for both the L_3 and L_2 components. This helps increase our confidence in both the self-absorption measurements and in the thin-film absorption data. Having confidence in the position of the L_3 edge is especially important because the Fermi energy is assumed to be at this position in discussions to follow.

As is well known, the absorption fine features within several eV of the edge should reflect information about the structures of the normally vacant electronic states. In the first transition series the lowest empty states are primarily of $3d$ character so that the $L_{2,3}$ or $M_{2,3}$ absorption spectra should contain this information. It is seen in Fig. 1 that there are three maxima (b, c, and d) observed just above the L_3 edge in Cr. In the only other recent study of the Cr L_3 absorption, Bonnelle[10,20] observed only a single broad maximum. If the three maxima shown in Fig. 1 are indeed related to the structure of vacant $3d$ states, then one might reasonably expect to see similar maxima in the $M_{2,3}$ absorption spectrum. Cr $M_{2,3}$ absorption has been reported by Agarwal and Givens[21] and Tomboulian *et al.*[22] Their results are compared with the L_3 absorption in Fig. 2. As can be seen, the two M spectra are not in very good agreement with each other although Agarwal and Givens's results are in fairly good agreement with the L_3 spectrum. One of the problems with the $M_{2,3}$ spectra is that M_2 and M_3 levels are separated by only 1 eV or so and the fine structure near the edge could be a combination of M_2 and M_3 absorption features. This problem does not exist in the $L_{2,3}$ spectra since the L_2 and L_3 levels are well resolved from each other as evident in Fig. 1. The fine features observed near the L_3 edge are further supported by comparisons which will be made later with theoretical band-structure calculations. From the curves in

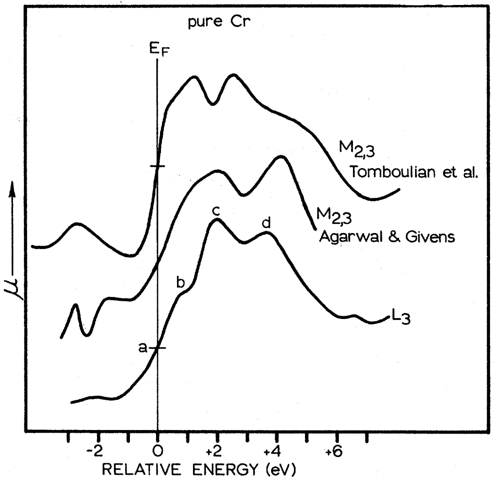

FIG. 2. Comparison of Cr L_3 absorption with $M_{2,3}$ absorption obtained by Agarwal and Givens (Ref. 21) and Tomboulian *et al.* (Ref. 22).

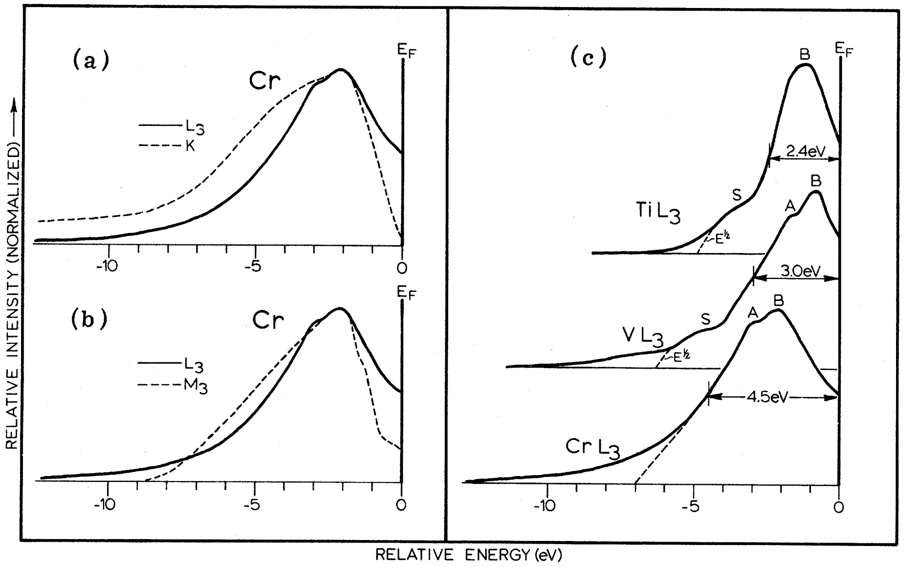

FIG. 3. (a) Comparison of Cr L_3 and Cr K (Ref. 24) emission bands. (b) Comparison of Cr L_3 and Cr M_3 (Ref. 9) emission bands. (c) Comparison of Cr L_3, Ti L_3 (Ref. 6), and V L_3 (Ref. 7) emission bands. Peak heights normalized.

Fig. 2 it appears that the $M_{2,3}$ absorption spectrum of Agarwal and Givens is to be preferred over that of Tomboulian *et al.* It is further noted that the Cr K absorption spectrum has been carefully recorded[23] and shows no evidence of fine structure within 5 eV or so of the edge. This lends more weight to the assumption that maxima b, c, and d in the L_3 spectrum are indicative only of structure in the vacant $3d$ states.

While the absorption spectra contain certain useful information about the vacant states, it is the occupied band states which are of primary interest in the transition metals, at least from the experimental standpoint. In studying the structure of vacant states one is fairly well restricted to SXS data. For the occupied states, however, a few newer techniques such as UPS, INS, and XPS, in addition to SXS, are available to the experimentalist. All of these techniques provide information related to the density of occupied states, but comparing the various results with each other is sometimes difficult. This is so because each technique involves different electronic transitions and different transition probabilities. Nevertheless, it can be instructive to compare SXS, UPS, INS, and XPS data for a given element as has been done recently for Cu.[5] In the case of the lighter $3d$ elements such as Ti, V, and Cr this cannot yet be done because no INS or XPS data on them has appeared. There are several SXS and UPS results available for Cr, however, and these will now be compared with each other and with some theoretical predictions.

As mentioned in the introduction, the generally accepted picture of the band structure of the first-series transition metals is one of a narrow $3d$ band of high-level density overlaying a broad $4s$-$4p$ band of low-level density. On this basis, one would expect the L_3 and M_3 emission bands to be very similar to each other but very different from the K band. The extent to which this is true in Cr is illustrated in Fig. 3.

In Fig. 3(b), the L_3 band obtained in this study is compared with the M_3 band of Skinner *et al.*[9] As can be seen, the bands agree in some respects but there are also some disparities. The M_3 band is less intense at the Fermi energy (E_F) than is the L_3 and may, in part, be due to self-absorption effects of which Skinner *et al.* made no mention. There are also two humps in the M_3 band to the high-energy side of the peak maximum which are not observed at all in the L_3 band. In addition, the M_3 band is somewhat broader at half-maximum and does not show the extended tailing observed in the L_3 band. Cuthill *et al.*[4] and Dobbyn *et al.*[5] showed similar discrepancies in the L_3 and M_3 bands of Ni and Cu and postulated that it was caused by the fact that $2p$ and $3p$ inner levels have quite different radial wave functions. If this is indeed the cause, then the same argument could be applied to Cr to explain the band differences in Fig. 3(b).

In Fig. 3(a) the L_3 band is compared with the K band published by Nemoshkalenko and Nagornyi.[24] Considering the different experimental conditions, instrumental resolution, inner-level widths, and inner-level wave symmetry, these bands are in rather good agreement. The K band should reflect primarily the distribution of $4p$ symmetry as opposed to the L_3-band reflection of $3d$ and $4s$ symmetry. Many theoretical treatments of the band structure of Cr and other transition metals consider the admixture of $4p$ states into the $3d4s$ band to be rather unimportant. However, the very fact that the K emission band and K absorption edge are observed and occur over the same energy ranges as the L_3 and M_3 spectra indicates that p states are probably admixed over the entire extent of the $3d4s$ band.

Concentrating now on the Cr L_3 SXS results, let us assume that the emission and absorption spectra of Fig. 1(a) are reliable and truly characteristic of pure Cr metal. What type of information about the energy-band structure can we reasonably expect to extract from these spectra? As discussed in the Introduction, we certainly cannot obtain directly the density of states as many investigators at one time believed. We can, however, hope to obtain some data which are related to the density of states. Primarily, the measurements of most interest would be (a) the position of the Fermi energy, (b) the total width of the occupied band states, and (c) the positions of certain maxima and minima in both the occupied and vacant portions of the density-of-states curve. Since the L_3 emission band, with the excitation conditions used in this work, has considerable satellite emission present at the L_3 edge, the edge itself is not observable. It will be assumed, though, that the emission and absorption edges coincide and that the absorption edge therefore determines the position of E_F. By using the edge position obtained in the self-absorption spectrum [see Fig. 1(b)], E_F can be accurately placed on the L_3 emission band.

The assessment of the bandwidth and importance of certain maxima and minima will now be handled in three stages. First, the Cr L_3 SXS band will be compared to the Ti and V SXS bands obtained previously. Then the SXS bands will be compared to UPS optical density-of-states curves. Finally, the spectra will be compared to some theoretical band-structure calculations.

In Fig. 3(c) are shown the SXS L_3 emission bands of Ti, V, and Cr. The Ti and V bands are the same ones shown in previous reports.[6,7] The two important points of comparison are the band shapes and bandwidths. In determining the width of a transition-metal L_3 band, certain simplifying assumptions must be made in measuring the position of the low-energy limit. The classical method of fixing this limit is to assume that the band tail follows the $E^{1/2}$ law for L spectra, and the $E^{3/2}$ law for K spectra. For the L_3 bands of most of the $3d$ metals, however, the low-energy tails do not follow this law because of the well-known extended tailing which occurs. This extended tailing is particularly evident in the Cr L_3 band and is probably due to a combination of effects such as Auger processes and other electron-electron interactions.[25,26] The method used here to approximate the bottom of this band is to extrapolate to background the linear portion of the low-energy slope. This extrapolation is indicated by the dashed line in Fig. 3(c). For Cr this extrapolation is rather straightforward but in the Ti and V bands there is an extra hump near the tail labeled S. The question arises as to what causes this hump and whether or not it should be included in the bandwidth measurement. In previous reports on Ti and V[6,7] it was suggested that this hump arises from $4s$ states with the main part of the band being representative of $3d$ states. This suggestion is further supported by the fact that when hump S is included, the measured bandwidth is in rather good agreement with theoretical predictions of the width of the occupied $3d4s$ band.[6,7] For the Cr L_3 band, no hump is evident at the tail so that any contribution to the spectrum which may occur from the $4s$ states cannot be definitely identified as such. There is no way of differentiating between possible $4s$ structure and the extended tailing which dominates the low-energy side of the emission band. It will be shown momentarily, however, that the bandwidth obtained by the linear extrapolation of the low-energy slope agrees quite well with the theoretical value for the occupied $3d4s$ width in chromium. The width of the d band alone will be seen to be approximated by the width at half-maximum of the L_3 band. The measured L_3 widths are listed in Table II and it is noted that these values are uncorrected for instrumental broadening and internal-level width. From the spectra of Fig. 3(c) it appears that the width of the occupied states increases in going from Ti to V to Cr in about the proportion calculated by Mattheiss.[27] It is also evident that the separation of the band maximum from E_F is different in each case. This is predicted by specific-heat measurements and will be discussed in more detail shortly.

The only other deep-band experimental studies, besides SXS, which have been reported for Cr are the UPS results of Lapeyre and Kress[28] and of Eastman.[8,29] Eastman also reports data on Ti and V.[8] The comparison between SXS curves and UPS optical density-of-states curves for Ti, V, Cr,

TABLE II. Energy measurements on SXS L_3 emission bands shown in Fig. 4. All values given in eV.

Element	Separation between E_F and emission maximum	Width at half-maximum	Full width
Ti	1.3	2.4	4.9
V	0.9	3.0	6.3
Cr	2.2	4.5	7.0
Fe[a]	1.2	2.8	~6

[a] See Ref. 15.

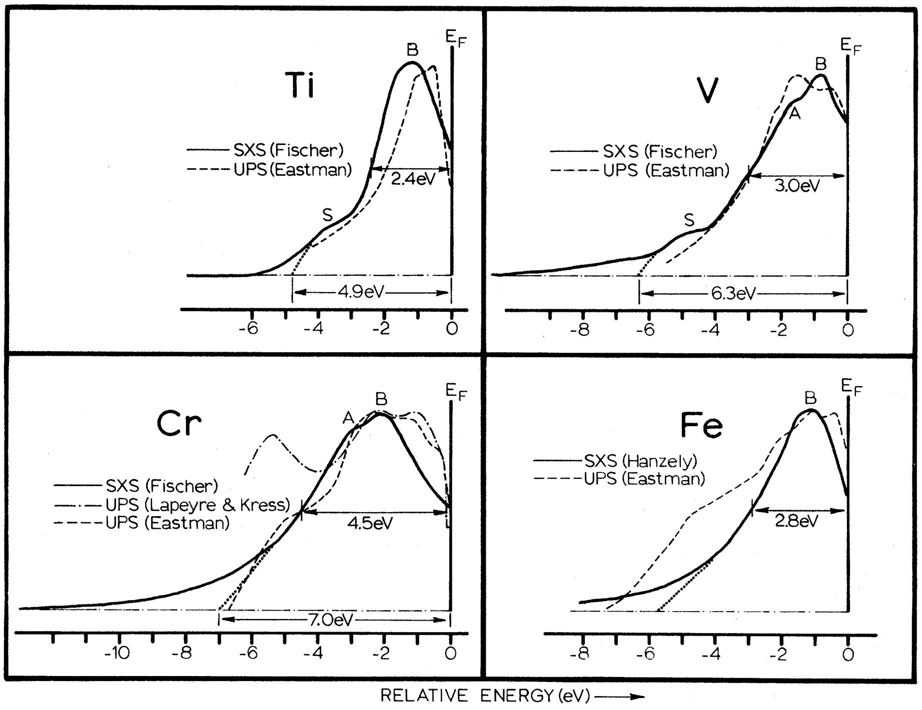

FIG. 4. Comparison of SXS L_3 bands and UPS optical density-of-states curves for Ti, V, Cr, and Fe. All curves normalized to same peak height. Ti, V, and Cr L_3 bands obtained by present author. Fe SXS from Hanzely (Ref. 15) and UPS from Eastman (Refs. 8 and 29) and Lapeyre and Kress (Ref. 28).

and Fe are given in Fig. 4. In comparing SXS and UPS results it must be kept in mind that they represent different excitation mechanisms and transition probabilities and therefore an exact matchup is not expected. The element of main interest here is Cr, but it is felt that the experimental results can be better evaluated by also having at hand the curves for its nearest neighbors in the Periodic Table. Also, the series V-Cr-Fe is of interest because all three elements have the same bcc structure. The Fe SXS L_3 band in Fig. 4 is taken from the work of Hanzely[15] and was obtained at threshold excitation. It will be noticed that the agreement between the SXS and UPS curves is not the same for each element. The best agreement is found for vanadium where the two curves have a similar shape and width with the main maxima at comparable positions and the same intensity at E_F. For Ti the two curves have about the same width but the SXS maximum is shifted to a lower energy. Also, there is no evidence of a maximum in the UPS curve at about -4 eV corresponding to hump *S* in the SXS spectrum. This hump is also absent in the V UPS curve but present in the SXS curve. Strangely enough, just the opposite phenomenon is observed for Cr and Fe where a low-energy maximum is observed in the UPS curve but not in the SXS. For Cr two UPS curves are shown, one from Eastman,[29] the other from Lapeyre and Kress.[28] They are in good agreement with each other except for the magnitude of the peak at about -5.5 eV. This peak is not present in the SXS curve and is not predicted by theoretical calculations.[30–32] A similar low-energy peak is observed in the UPS curve for Fe, but not in the SXS curve or in the theoretical predictions. Since Eastman[29] found that a similar anomalous peak which had been reported in the UPS optical density of states of Ni and Co was due to spurious surface effects, one might wonder whether this peak in the Cr and Fe curves is also anomalous and not truly characteristic of the density of states. There are also peaks in the UPS curves from Cr at about -0.4 and -1.0 eV which are not observed in the SXS curve. Good agreement is found, however, on the position of the most intense peak, on the intensity at E_F, and on the bandwidth. Because of the different information carried in UPS and SXS data, it is difficult to judge how meaningful the discrepancies are.

Another point of interest concerning the SXS L_3 bands in Fig. 4 has to do with the separation of the peak maximum from E_F. The measured values are listed in Table II. They are found to be in good agreement with specific-heat measurements of the density of states at E_F.[33,34] This is especially evident for Cr where specific-heat measurements indicate that E_F falls at a minimum in the density of state. The SXS L_3 emission and absorption curves clearly support this.

Three of the elements represented in Fig. 4 crystallize in the bcc structure. There has been some discussion in the literature as to whether or not the rigid-band model can be used to describe their en-

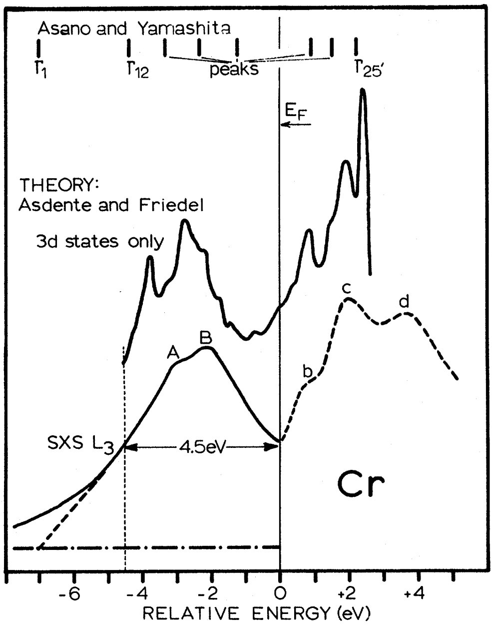

FIG. 5. Comparison of Cr SXS L_3 emission and absorption curves with calculated 3*d* density of states from Asdente and Friedel (Ref. 30) and with band-structure results of Asano and Yamashita (Ref. 32).

ergy-band structure. In going from V to Cr, the SXS L_3 bands could be roughly described as indicating the same structure with E_F shifted by about + 1.3 eV. This is in agreement with the rigid-band model. When moving to Fe, however, the L_3 band does not show the expected form. This would indicate that the rigid-band model does not apply.

Let us now compare the Cr SXS L_3 emission and absorption curves to some theoretical predictions. Energy-band calculations for Cr have been reported by Asdente and Friedel,[30] Lomer,[31] Mattheiss,[27] and Asano and Yamashita.[32] Only Asdente and Friedel, however, show a density-of-states curve but their calculations involved only the 3*d* states with no 4*s* hybridization. Their results are shown in Fig. 5 and compared to the SXS L_3 curves. In certain respects there is quite good agreement between the two. Peaks *A* and *B* in the emission band and peaks *b* and *c* in the absorption curve match up nicely with peaks in the density of states. Also, the Fermi energy is in a trough in both cases. There is nothing in the emission band, however, to correspond to the calculated peak at about − 3.8 eV. Also, peak *d* in the absorption spectrum has no counterpart in the calculated structure although its position is confirmed by the M_3 absorption spectrum (see Fig. 2). The width at half-maximum of the emission band corresponds quite well to the calculated width of the occupied *d* states. The total L_3 band, however, extends farther to lower energy than the calculated structure which may, in part, be due to the contribution of 4*s* states which were not considered in the calculation. Asano and Yamashita,[32] however, did include the 4*s* states in their calculations [Korringa-Kohn-Rostoker (KKR) method] and obtained a total width of occupied states of 7.0 eV. This is in excellent agreement with the full L_3 bandwidth determined by the linear extrapolation of the low-energy tail. Such close agreement in bandwidths may indeed be fortuitous, but it may also indicate that the 4*s* states do contribute somewhat to the low-energy tailing. Although Asano and Yamashita did not show a density-of-states curve, certain prominent features of such a curve can be inferred from their energy-band calculations. These features include the bottom of the *s* states (Γ_1), the bottom of the *d* states (Γ_{12}), the top of the *d* states ($\Gamma_{25'}$), and the most prominent peaks. Their energy positions are indicated by vertical lines at the top of Fig. 5. It is seen that the *d*-states' features are in rather good agreement with the results of Asdente and Friedel. The various bandwidth measurements are summarized in Table III.

IV. SUMMARY

The chromium SXS $L_{2,3}$ emission and absorption spectra have been recorded and discussed in relation to the energy-band structure. Results were evaluated by comparing the L_3 spectra with the SXS $M_{2,3}$ and *K* bands, with UPS optical density-of-states curves, with theoretical band structures, and with comparable studies on Ti, V, and Fe.

In several respects there appears to be reasonably good agreement between theory and the various experimental results. The over-all picture that is suggested for Cr is one of a 3*d* band having an occupied width of about 4.5 eV overlapping a broader 4*s* band which extends to around 7 eV below E_F. Both theory and experiment agree that the Fermi energy is at a minimum in the density of states. There is a tolerable matchup between most maxima

TABLE III. Width of occupied states in pure Cr. All values given in eV.

Calculated	3*d*	3*d*4*s*
Asdente and Friedel (Ref. 30)	4.5	⋯ (tight-binding approximation)
Lomer (Ref. 31)	4.0	8.1 (APW method)[a]
Mattheiss (Ref. 27)	4.2	8.0 (APW method)
Asano and Yamashita (Ref. 27)	4.4	7.0 (KKR method)
Mattheiss (Ref. 35)	⋯	6.9 (APW method)
Experimental	Width at half-maximum	Full width
SXS L_3 (present work)	4.5	7.0
UPS (Ref. 8)	~4	~7

[a] Augmented-plane-wave method.

and minima in the SXS curves and density of states but there are also some discrepancies. Over-all, however, the agreements are most encouraging. The disagreements which occur are primarily in the fine features and are not considered as being particularly serious at the present state of the art.

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Magnetoresistance Study of Open Orbits in Gallium†

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The results of an extensive investigation of the magnetoresistive properties of gallium are presented. It is found that the Fermi surface of gallium is topologically open in the $\vec{k}_x$ and $\vec{k}_z$ directions. At least five different open-orbit regions are found; of these, several apparently result from the effects of magnetic breakdown. The consistency of the data with recent pseudopotential calculations is discussed.

I. INTRODUCTION

Although considerable experimental and theoretical work has been performed over a period of several years in an attempt to understand the Fermi surface and electronic band structure of gallium, a consistent picture has only recently been achieved by Reed's pseudopotential analysis.[1] An extensive bibliography and discussion of this previous work is contained in Reed's paper and will not be included here.

The results of a complete investigation of the magnetoresistive properties of gallium are presented in this paper. The data reported here have been summarized in Reed's paper together with an analysis which shows that it is compatible with his Fermi-