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THE VALENCE BANDS OF Cr-RICH Fe-Cr ALLOYS
DETERMINED BY X-RAY PHOTOELECTRON SPECTROSCOPY

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The valence bands of Cr-rich Fe-Cr alloys
determined by x-ray photoelectron spectroscopy

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ABSTRACT

The valence bands of Cr-rich Fe-Cr alloys determined by
x-ray photoelectron spectroscopy

The valence bands of Cr-rich Fe-Cr alloys were examined by x-ray photoelectron spectroscopy for the possible existence of a virtual bound state. Samples containing 1%, 4%, 12%, and 21% Fe were tested, and compared with a theoretical calculation based on the VBS model. Final results showed a trend possibly indicative of a VBS in this system, but further data of higher resolution is needed for quantitative results.

THEORY OF ALLOYS AND THE VBS MODEL

In an effort to understand and predict the electronic, magnetic, thermal, and optical properties of a simple metal, it is necessary to determine the eigenfunctions and eigenvalues of the electrons of that metal. This is easily done if the lattice potential is periodic, as it is in the simple metals. Once the wavefunctions and allowed energies are known, such properties as the metal's resistivity, susceptibility, specific heat, and dielectric functions can be determined, as well as a host of other useful information.

Once the periodicity of the lattice is disturbed by the addition of impurities or by alloying, the once-easy task of determining E and Ψ becomes nearly or totally impossible. Thus most of the properties that are in principle calculable for a pure metal are no longer exactly determinable. Only by various approximations beyond those employed for pure metals can any of these properties be determined. There are many such approaches to determining the electronic structure of alloys and impure metals, each yielding different properties and each having various degrees of success.

In general, if the density of states of the alloy can be determined, several thermal and electromagnetic properties can be obtained or interrelated. Several methods have been proposed for calculating densities of states in these metals,

among which are the Thomas-Fermi Model (TFM), the virtual crystal approximation (VCA), and the virtual bound state (VBS) method of Friedel (1958, 1963), Anderson (1961), and others (Wolff 1961).

The Thomas-Fermi model uses a screened impurity atom potential as a perturbation on the electrons in the host metal. It assumes the conduction electrons of the matrix screen the Coulomb field of the impurity atom, yielding the potential

$$V(r) = \frac{-\Delta Z e^2}{r} e^{-r/\lambda} \quad (1)$$

where λ is the screening length and ΔZ is the difference in the number of valence electrons of the two types of atoms present. For dilute transition metal alloys, $V(r)$ is a small perturbation with highly localized screening ($\lambda \sim 1 \text{ \AA}$), and the TFM yields good results (Friedel 1958). However, this method fails if the concentration of impurities increases, or $V(r)$ becomes too large for perturbation theory to apply. Also, the larger ΔZ , the larger the phase shift due to scattering. The TFM breaks down and calculations based on scattering theory are needed.

The virtual crystal approximation assumes a perturbing crystal potential that is a linear combination of the impurity and matrix atom potentials, proportional to their concentrations. The VCA further assumes equal electron

wavefunctions about both matrix and impurity atoms. This is not the case for any alloy, especially if any local charging or screening takes place. The VCA also fails to account for the formation of localized magnetic moments as found in several alloy systems.

The virtual bound state can be thought of as a resonance phenomenon at the site of an impurity atom. The d state electrons of the impurity atom interact with the conduction electrons of the matrix in the following simplified manner. Picture a free electron at the site of a spherically symmetric impurity potential $V(r)$ as in Figure 1a. If $V(r)$ were deep enough (dashed lines) the electron would have a bound state energy of E_ℓ . But $V(r)$ is too shallow for a bound state of that energy so the electron state lies in the continuum. As the ℓ -th harmonic interacts with the conduction electrons whose energies are near its own E_ℓ , new states are formed whose energies in turn are near E_ℓ , which then interact with other electrons. Eventually the electron state broadens about the impurity, and a virtual bound state forms, as shown in Figure 1b.

In a matrix whose valence differs from that of the impurity atom, $V(r)$ lies above or below the matrix potential $V'(r)$ as shown in Figure 2. If $V(r)$ is larger about the impurity, a bound electron at the impurity site of energy E_d could tunnel into the conduction band of the matrix

(shaded area), broadening its state with a certain lifetime. If the valence of the impurity atom is greater than that of the matrix atom, $V(r)$ would be less than $V'(r)$, and additional bound states below the conduction band of the matrix would form.

Several different methods have been used in the development of the VBS theory. Friedel used phase shift analysis, Anderson includes the Coulomb repulsion of electrons with anti-parallel spin, while Wolff relates the previous two methods, deriving the repulsion term used by Anderson by scattering electrons from the impurity potential.

The Friedel method is straightforward, beginning with a free electron and $V(r)$ about the impurity. For d band transition elements we consider $\ell = 2$ phase shifts only, as they contribute the most. $V(r)$ perturbs the wavefunction of the free electron, producing a phase shift δ at large distances from the impurity. If the electron were bound, δ would have an initial value of π for an energy near the bottom of the conduction band E_c (Figure 3). As the electron's energy increases through E_d , the energy at the center of the VBS, δ would approach zero. But in the VBS model, δ begins at zero, and joins the phase shift curve for the bound state at higher energies. The energy range in which δ increases is related to the width W of the VBS.

The electronic density of states is increased by a

small $\delta D(E)$, a lorentzian distribution centered about E_d of width W according to Equation 2,

$$\delta D(E) = \frac{c}{V\pi} \frac{2(2\ell + 1)}{W^2 + (E - E_d)^2} \quad (2)$$

where c is the concentration of the impurity and V is the atomic volume of the alloy (Friedel 1963). The factor $2(2\ell + 1)$ enters as the multiplicity of the ℓ -th state.

One problem with the theory is that the contribution of the VBS to the electron $D(E)$ is too large. The VBS has fewer electrons than a true bound state as δ is always less than π , as is the case for a true bound state. However, the model does hold well for E_d near E_F , the Fermi energy of the alloy.

The model also predicts a residual electrical resistivity due to the scattering of electrons with energies near E_d . As $\delta D(E)$ peaks about E_d , the residual resistivity should show a similar peak. By phase shift analysis, a relationship is obtained between the residual resistivity $\Delta\rho$, the concentration of the impurity atoms c , the valence of the matrix atoms p , and the Fermi wave vector k_F . This has a maximum value of

$$\Delta\rho_{\max} = \frac{20\pi c}{p k_F} \quad (3)$$

for d electrons when E_d lies at E_F for a half filled VBS (Friedel 1958).

A magnetic moment formation is also predicted, if d-d exchange effects are considered. The VBS splits in two, one half of spin up electrons, the other of spin down (Figure 4). Hund's rules predict that they will fill one at a time, the state of lower energy first, leading to a localized moment in the alloy.

Anderson's model treats the d-d exchange splitting of the VBS not as an "exchange" effect, but as a result of the repulsive force between anti-parallel spin electrons at the impurity atom site. Two VBSs are formed as in the Friedel model: one of the spin up, the other of spin down. If the spin up states of energy E_d at the impurity are assumed full, an electron of spin down and energy E_d below E_F sees the repulsion, and its energy shifts upward by an amount U , the repulsive energy. This electron energy now lies above E_F , and this state then is empty. One VBS at E_d is full, the other at $E_d + U$ is empty. As the number of d electrons in the crystal increases, U decreases. As the two states near each other in energy, the moment collapses and the two states become one.

Anderson's Green's function method leads to expressions for W and $\delta D(E)$ that are similar in form and reducible to those found by Friedel (Anderson 1961).

$$W = \pi \langle V^2 \rangle_{\text{avg}} D(E_d) \quad (4)$$

$$\delta D(E) = \frac{1}{\pi} \frac{W}{W^2 + (E - E_d)^2} \quad (5)$$

In Equation 4, $\langle V^2 \rangle_{\text{avg}}$ is the average s-d scattering matrix element, or the energy of interaction of the d electrons with the conduction electrons.

Wolff uses a Hartree-Fock calculation of the scattering of 4d electrons by the impurity potential to arrive at similar results in his model of the VBS. The VBS corresponds to a maximum in the scattering cross section for the electrons by the impurity, and if the maximum is sharp, W small, and E_d lies near E_F , a moment will form due to the exchange or repulsive force term U between anti-parallel spin electrons. Wolff's results (Wolff 1961) for W and $\delta D(E)$ are of the same form as Anderson's and Friedel's.

The three different methods give the same results for the VBS. In all three models the VBS is found to be lorentzian in shape, and of similar width. More recent and more rigorous calculations (Riedinger 1971) have indicated the VBS is not purely lorentzian in shape, but is somewhat skewed with a sharp edge at the high energy side of E_d . From each of these models it is possible to predict the formation of localized magnetic moments, changes in residual resistivity, susceptibility and other properties of alloys such as specific heat.

Anderson assumes the d electron states in the conduction band to be different from the electron state on the impurity, while Wolff assumes the impurity electron to be of the conduction band, and therefore equivalent. Thus the Anderson method is more applicable to alloys of elements of the early 3d series, while Wolff's method is better applied to alloys of elements near the end of the series. None of these various approaches to the VBS are exactly applicable to transition metals alloyed with other transition metals, due to additional band hybridization and interactions, and a more troublesome structure in general, though their basic ideas and theory can be carried over to these metals (Lomer 1963).

The problem of the VBS in transition metal-transition metal alloys is complicated by both the overlapping effect of the d bands of the constituents, and their proximity to E_F . As can be seen in Equation 4, the width of the VBS is directly proportional to both the density of states of the alloy at E_d , and the amount of interaction between the impurity electron and the host conduction electrons (Clogston 1962). If $D(E_d)$ is large as in the case of transition metal hosts where the host d band lies near both E_d and E_F , d-d interaction between host and impurity electrons would be strong, the width of the VBS large, and the VBS might be difficult to detect by experiment. For impurities in noble metals, the host d band lies far enough

below E_F and impurity d electrons that d-d interaction between host and impurity is weak. In this case $D(E_d)$ is small, primarily that of the s band of the host. W is small as well, and the VBS is relatively sharp and distinct.

Depending on where the center of the VBS lies in the host $D(E)$, the width of the VBS and its detection limit will change. A host such as Cr has a minimum in its $D(E)$ near E_F (Figure 12). If a VBS formed there it might be detectable. If on the other hand, it formed in the Cr d band, it might not be seen due to its resulting broadness.

EVIDENCE SUPPORTING THE VBS MODEL

Until recently, the bulk of the experimental evidence supporting the existence of the VBS has been of an indirect nature. Neutron scattering, magnetic susceptibility, specific heat, and residual resistivity measurements have long been used to support the model. A large number of reviews of these various experiments and data exist, pertaining to many different alloy systems (Heeger 1969, Daybell and Steyert 1968, Van den Berg 1964, et al.). Only in the past few years has the use of x-ray photoelectron spectroscopy on these materials (Hüfner, Wertheim, and Wernick 1973), a method to be discussed in the next section, made it possible for more direct measurement of the contribution of the VBS to the electronic density of states.

Residual resistivity measurements have shown the presence of the VBS in Al-rich Al-transition metal alloys. In the 3d series, Ti has an empty d shell above the Fermi level of Al, while Ni and Cu have full d shells below E_F of Al. As the transition metal series is alloyed with Al, from Ti to Ni, the d band of the impurity is progressively filled. As these d electrons mix with the Al conduction electrons, a VBS is formed. A maximum in $\Delta\rho$ is found near Cr in the middle of the series, where half the d shell of the impurity has crossed below the Fermi level (Figure 5). Experiment

indicates that $\Delta\rho_{\text{max}}$ is nearly equal to Friedel's prediction. This is further demonstrated with 3d impurities in Zn. For impurities in Au, one expects two peaks in $\Delta\rho$ as the two separated VBS levels pass below the Fermi level at different points in the transition metal series. Such an effect has also been seen (Heeger 1969).

A similar effect is expected and observed in specific heat data. If the VBS contribution to the electronic specific heat is impurity concentration dependent, it should yield a maximum when the impurity d band is half full, or when E_d is located at E_F (Friedel 1963).

The highly localized nature of the VBS as evidenced by the magnetic moment phenomenon has been effectively shown by neutron scattering experiments (Lomer 1963). The form factor for scattering due to the magnetic moment is nearly the same as that due to the impurity atoms themselves, in Ni-rich Ni-Fe alloys, even to very high impurity concentrations.

Infrared and visible absorption measurements on many of these systems have shown some evidence for the VBS. These are nearly direct measurements of the increased density of states and the VBS itself, but the spread in final states is enough of a problem that exact quantities are difficult to obtain. However, an impurity-concentration dependent peak in the absorption is seen between 0.5 and 0.8 eV in Au films

with Ni as the impurity. Transmission and reflection measurements on Pd and Mn impurities in the noble metals (Myers, Walldén, and Karlsson 1968) also show peaks at about 2.6 eV below the Fermi edge. Recent optical studies on 3d transition metals alloyed with Ag (Koike, Yamaguchi, and Hanyu 1975) have shown further evidence for, and supported previous conclusions about the VBS in noble metal-based alloys.

Various photoemission experiments on Ag-Pd and Cu-Ni systems show the existence of a VBS over great impurity concentration ranges, up to forty percent. Manganese in Ag shows two VBS peaks about the Fermi edge, separated by 5 eV. The peaks as well as their separation were predicted by a VBS model (Heeger 1969).

Hüfner, Wertheim, and Wernick have shown by XPS measurements the existence of the VBS in various noble metal alloy systems (Hüfner, Wertheim, and Wernick 1975). Taking XPS spectra of both the pure noble metal and the alloy, then normalizing them and subtracting one from the other, the contribution to the density of states from the VBS is clearly seen. This method does not directly yield a true density of states though, as the data obtained in XPS represents a convolved density of states as modified by the instrument used, often causing considerable loss in resolution. Various deconvolution techniques have been proposed

(Ebel and Gurker 1974, Wertheim 1975), though deconvolution of the XPS data is unnecessary to simply see the effect of the VBS.

THEORY OF X-RAY PHOTOELECTRON SPECTROSCOPY

The analysis of photoelectrons excited by electromagnetic radiation is a useful experimental method for directly determining the electronic density of states of many materials. By far the most commonly used technique is x-ray photoelectron spectroscopy (XPS), which usually employs the $K\alpha$ emission lines of Mg and Al, located at 1253.6 and 1486.6 eV respectively, each having a natural linewidth of approximately 0.8 eV (FWHM). Other elements besides Al and Mg can be used for the production of x rays, but they are seldom employed as their linewidths increase with their atomic number (Hagström and Fadley 1974). Ultraviolet photoelectron spectroscopy (UPS) often used He-I and He-II radiation at 21.2 and 40.8 eV respectively, with a linewidth of 0.3 eV (FWHM). Synchrotron radiation provides a continuum source between 10 and 10,000 eV, requiring the use of a monochromator.

An important consideration in selecting a method is the penetration depth of the incident radiation, or the escape depth of the photoelectrons. The more energetic the radiation, the greater the escape depth of the photoelectrons, as can be seen in Figure 6. The presence of any oxide or contaminant atoms on the surface is critical (far more so for UPS than XPS); a few monolayers of oxide could

mask the UPS spectrum entirely. The incidence angle of the radiation is also important. At shallower angles, more surface electrons and fewer bulk electrons are emitted.

The sample to be studied is mounted in a high-vacuum chamber (10^{-7} - 10^{-11} Torr) to reduce the flux of contaminating atoms striking its surface. Once photoelectrons have been excited, they are energy analyzed by electrostatic and/or magnetic fields so only electrons with specific energies are collected and counted by the electron-multiplier tube in the analyzer.

The photoelectrons obey Equation 6 below, where $h\nu$ is the energy of the incident radiation, B.E. is the binding energy of the electrons in the sample, K.E. is the final kinetic energy of the photoelectrons, and W.F. is the work function of the spectrometer (Figure 7).

$$h\nu = \text{B.E.} + \text{K.E.} + \text{W.F.} \quad (6)$$

The work function is a complicated quantity, dependent upon the composition of the sample chamber walls, and the amount of surface contamination present. Thus it shifts as the condition of the walls and chamber change (Carlson 1975).

Another difficulty encountered in XPS is the presence of satellite emission lines as well as the principal $K\alpha$ lines of Mg and Al. A certain amount of bremsstrahlung present produces a broad background excitation of the sample

as well. The use of a monochromator eliminates most of the unwanted radiation and reduces the linewidth of the primary emission line by as much as a factor of four. In so doing it also severely reduces the intensity of the radiation (Carlson 1975).

Line broadening of the spectra can be a problem in XPS, and is basically due to two mechanisms. The first is the finite lifetime of the holes formed in both the x-ray target and the sample being studied. In the former, photon broadening occurs which can be partially overcome by use of a monochromator. In the latter, the width of the photoelectron's spectral line increases with binding energy. Valence electron final states are of a longer lifetime than those for core electrons. Hence valence band $D(E)$ features can be sharper than core level features. They are of such narrow widths however, that without very high resolution they cannot be discerned by XPS. The second type of broadening arises in alloys from the scattering of electrons by the compositional disorder. This can shorten the lifetimes of valence band holes, leading to a broadening of structure in the valence band density of states.

EXPERIMENTAL DESIGN

Transition metal alloys have not been well-studied with respect to the possible presence of a VBS. As mentioned earlier its detection in these alloys could be very difficult. A VBS has been suggested by magnetic, electrical, and optical experiments in the Fe-Cr alloy system (McCain and Schröder 1969, Suzuki 1966). In addition the samples were available for immediate study. It was for these reasons that Fe-Cr alloys were chosen for XPS study of their valence band in an effort to identify a VBS. XPS was chosen over UPS due to the much reduced effect oxides have on XPS spectra.

The equipment used for the XPS measurements was an AEI ES200 electron spectrometer with a double focusing hemispherical electrostatic energy analyzer. A Nicolet Model 1180 Data System was interfaced with the spectrometer to control data compilation, storage, and manipulation. A He atmosphere glove box sample preparation chamber provided a more stable atmosphere in which to prepare the samples before insertion into the spectrometer. Equipped with Ti furnace and molecular sieves, it reduced both O_2 and H_2O to less than one ppm.

An argon ion gun was used for in situ sputter-cleaning of the sample surfaces, the operation of which is described below.

A 130W Mg x-ray tube was used with a maximum power output of 450W, and linewidth of approximately 0.8 eV.

The Cr-rich Fe-Cr alloys were produced by an arc-zone melting process and cut to the proper size for the experiment, approximately 10 mm x 7 mm x 1.5 mm. A microprobe analysis was used to determine the exact composition of the samples as shown in Table 1. They were then abraded in the glove box until smooth and inserted into the spectrometer.

Table 1. Composition of samples as determined by microprobe analysis (Lynch, Rosei, and Weaver 1975)

Starting Composition	Actual	Crystal
1.0% Fe	1.0% Fe	single
5.0% Fe	4.0% Fe	5 mm grains
10.0% Fe	12.0% Fe	1 mm grains
20.0% Fe	21.0% Fe	3 mm grains

All samples underwent the same etch with research, grade Ar for seventy minutes at a pressure of 5×10^{-5} Torr. The current and voltage of the sputter gun and the temperature of the samples were raised during the etch from 15 mA, 0.5 kV and 30°C to 25 mA, 5.0 kV, and 200°C. Surface contaminants such as C and O were removed by the etch as observed by monitoring the C and O 1s XPS lines. Slight oxide and carbide layers remained that had been present before the etch was begun. While O remained negligible, C

did build up on the samples during the data runs, presumably from the residual hydrocarbons in the chamber or on the probe in the form of solvents or fingerprints. At all times during the data acquisition the pressure remained in the $5-8 \times 10^{-8}$ Torr range, as measured by a Granville-Phillips ionization gauge.

Changes in sample composition during the etch were monitored by looking at the 3p lines of Cr and Fe. The 12% and 21% Fe samples were not altered to any determinable degree by the etch, but the 4% Fe sample did in fact show signs of preferential etching. Iron core levels in this sample were diminished in intensity by the etch, to the extent that there was a question as to the presence of any Fe on the surface. A possible explanation could be the fact that the x rays sampled only a small percentage of the total sample area, and it is quite possible that only one or two grains in this sample were being measured. Iron could have been etched preferentially from the grains if particular crystal planes were exposed to the etch. A lighter etch was used on this sample.

EXPERIMENTAL RESULTS AND DISCUSSION

The actual data collected are shown in Figures 8-11. Each graph has the XPS spectrum of both the pure Cr sample and the alloy sample, with a difference spectrum given below. In all cases the Cr data are the same, the sum of all the XPS spectra of the pure sample taken over a period of several weeks. By the addition of the data in this manner the signal-to-noise ratio or statistical soundness of the data is reinforced. In each of the figures the spectra were normalized by a combination peak-height and area match. The pure Cr spectra were then subtracted from the various alloy spectra to obtain the difference spectra. Only part of the latter are shown, as there are no features to be seen in the region above 7 eV, that being a region of background counts from scattered electrons.

Subtraction of background counts from these scattered electrons poses a problem that should be mentioned at this point. It is assumed that the number of electrons scattered at a particular energy is proportional to the number of electrons whose energies are greater than those scattered. Some procedure must be devised for subtracting off a decreasing number of counts with decreasing binding energies - a nonlinear curve across the d band at best. If it is assumed that all the counts from the far left of the spectra

shown in Figures 8-11 down to about 8 or 9 eV are background, whatever procedure is chosen must subtract off all the counts in that region, and a decreasing number until the Fermi edge is reached, when the number of scattered electrons falls to zero. The fitting to match these end points at 7 eV and 0 eV is tedious, especially since the scattered count rate is not of a constant slope in that region, but instead depends on the area of the curve above it. It must be computer fit for each spectrum. A complex procedure has been worked out for this subtraction (Fadley and Shirley 1970) involving large matrices and much computer work. This was not performed on these spectra; the basic information about the VBS should not be drastically altered by that subtraction, as it is on the low energy and low scattered electron count side of the primary d band peak (Hüfner, Wertheim, and Wernick 1973).

The normalization of curves by matching peak heights or areas is also a problem. Peak height alone should not be used, as it is the area that is indicative of the number of electrons being sampled, and not solely the count rate at one energy. The area should be scaled by a certain amount if it is used, as more electrons are present in Fe-Cr samples than in pure Cr. Because scattered electron counts remain in these data, the area method becomes difficult. Thus a combination of the two methods is needed in which area and peak height and scattered electron counts are all

three balanced to reach a compromise.

According to the VBS model, the peak in or contribution to the density of states of Cr due to the VBS should increase in prominence and magnitude with increasing Fe concentration. The shift in prominence of the shoulder near 1 eV in the Fe-Cr spectra with increasing impurity concentration is quite evident in the 4%, 12%, and 21% samples. What was simply a shoulder in the pure Cr spectrum becomes a prominent peak by the time 21% Fe is reached.

It can be seen that there is no noticeable broadening of the primary d band peak as Fe concentration increases; it remains approximately 7 eV wide. Although Fe has its d band peak at about 1 eV (cf. Figures 12 and 13), a simple superposition of pure Fe $D(E)$ and pure Cr $D(E)$ in the proper ratio is not acceptable as an explanation for the spectra of Fe-Cr alloys. Although the shoulder-to-peak effect could be explained spectrally in this manner, physically that picture is incorrect. Complicated electron-electron interactions take place in the pure metals as well as in the alloys. Interactions between d electrons and d and s electrons take place in both metals which are complicated by the addition of one to another. There are unequal contributions to the $D(E)$ of the alloy from all of the bands of the Fe impurities. Also a lack of overall broadening of the peaks with increased Fe concentration rules out in part the possibility of a

simple overall peak broadening effect related to the different relaxation times of Cr and Fe electrons as would be expected if the above superposition were assumed.

In the 1% data there is a steepened Fermi edge which could be attributed to the $\delta D(E)$ of a VBS. The high energy side of the Cr peak is eroded away, possibly due to oxides or carbides on the surface preventing a good sampling of the bulk crystal. The lack of an oxygen peak in the valence band scan however tends to limit this possibility. The difference spectrum shows the addition to the shoulder, plus a dip in the density of states between 2 and 6 eV. Such a dip has been predicted for the VBS model (Riedinger 1971) as resulting from a realignment of d electrons in the host when the impurity atom is introduced. Caution should be taken in placing much emphasis on such a dip as being solely indicative of a VBS. Due to the presence of the scattered electron counts in this region, the ratio of scattered to unscattered counts increases with binding energy, and so the reliability of such difference spectra in general decreases with the distance from E_F .

Again with the 4% Fe sample, the shoulder has an increased height over that of pure Cr, and the difference spectrum shows the same basic structure as did that of the 1% alloy.

Upon reaching 12% Fe, the shoulder has separated to

form a separate peak, a feature which was reproducible from run to run. The difference spectrum for this sample is perhaps more statistically reliable than the previous two as the count rates were higher for the 12% alloy. It etched cleaner than the others, and the main Cr peak lined up better for this alloy as well.

Once the Fe concentration reaches 21% as in Figure 11, the shoulder of Figure 8 has become the prominent peak. The Cr peak lines up well here, and these data are probably the best statistically of any shown. The difference spectrum clearly shows the additional peak due to the Fe impurity.

The contention here is that the evidence provided by XPS indicates the existence of a VBS in Cr-rich Fe-Cr alloys. A theoretical calculation was performed by adding to a Cr $D(E)$ a lorentzian VBS in various proportions corresponding to the various Fe concentrations of the samples used, and then convolving the sum with a gaussian of half width 0.8 eV, the supposed width of the Mg $K\alpha$ line. The same trend was seen in these (Figure 14) as has been shown in the data from the XPS measurements. A shoulder at E_F grew with concentration to a position of dominance over the primary Cr d band peak. The problem of relating the convolved theory to the actual spectra is complicated however. The proper convolution requires knowledge of the spectrometer function. Use of a poisson, lorentzian, or gaussian function changes the

effects seen in the smeared $D(E)$. A good measurement of the instrument function for this spectrometer has not yet been made.

Some possible sources of error have already been mentioned. The fact that only a few grains of the sample are being measured introduces error if the grains are inhomogeneous, both from one grain to another, and within themselves. The x-ray beam intensity can fluctuate, lowering the count rate for part of a spectrum during one or more scans. Oxides which are exceedingly tough on these alloys alter the spectra, decrease the count rates, and lower the reliability of the data. Scattered electron counts in the data blur some features, and contribute large errors to the difference spectra above E_F . Not the least of these errors is introduced by the relatively large resolution width of the spectrometer during the scans. Curve normalization also is a source of error, as mentioned.

CONCLUSIONS

In conclusion, nothing specifically quantitative can be said concerning the data contained in Figures 8-11. Although the standard deviation of the data after smoothing is always less than that expected from the count rate (inversely proportional to its square root), and the major features are larger than that deviation, it is not good enough to determine the width W of the VBS, or the exact location of E_d with respect to E_F . This alloy system deserves a closer and longer look for actual quantitative data on its VBS. It is the author's feeling that ample evidence has been shown to warrant the continued study of the Fe-Cr system, specifically with monochromated x rays for higher resolution. If the installation of an ultra-high vacuum preparation chamber on the spectrometer is effected, the samples can be abraded under high vacuum conditions, to hinder oxide formation. It would then be possible to avoid etching the samples and the possible alteration of local compositions accompanying such etching, and to use UPS to examine the same energy regions as examined here with XPS. With the high resolution afforded by UPS, quantitative data can be obtained, and W and E_d determined for this system.

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APPENDIX: FIGURES

Figure 1. Real bound state (dashed curve of (a)) and virtual bound state (shaded area of (b)) formed about $V(r)$

Figure 2. Impurity atom d state overlapping host conduction band (a), and below host conduction band (b) (Sellmyer, to be published)

Figure 3. Phase shift δ for bound state (dashed curve) and VBS (solid curve) (Friedel 1963)

Figure 4. Magnetic moment formation by filling split VBS in (b). No moment is formed in (a) (Sellmyer, to be published)

Figure 5. Residual resistivity $\Delta\rho$ for Al-X alloys (Friedel 1963)

Figure 6. Escape depth of photoelectrons as a function of photon energy (Lindau and Spicer 1974)

Figure 7. Energy level diagram for photoelectron process

Figure 8. XPS spectra of Cr+1%Fe and pure Cr samples with difference spectrum below

Figure 9. XPS spectra of Cr + 4%Fe and pure Cr samples with difference spectrum below

Figure 10. XPS spectra of Cr+ 12%Fe and pure Cr samples with difference spectrum below

Figure 11. XPS spectra of Cr+21%Fe and pure Cr samples with difference spectrum below

Figure 12. Theoretical density of states for Cr, courtesy of B. N. Harmon (Department of Physics, Iowa State University)

Figure 13. Theoretical density of states for Fe
(Kowalczyk 1976)

Figure 14. $D(E)$ of Cr with a VBS added at 0.5 eV of halfwidth 0.45 eV for different concentrations of impurity. Convolution was with a gaussian of halfwidth 0.8 eV. Cr $D(E)$ courtesy of B. N. Harmon