THE FERROMAGNETIC TO PARAMAGNETIC PHASE TRANSITION OF Fe STUDIED BY X-RAY PHOTOELECTRON SPECTROSCOPY[*]

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ABSTRACT

Valence band x-ray photoelectron spectra from Fe(100) have been measured as a function of temperature to above the Curie temperature, T_c. The room temperature data can be reconciled with the theoretical one-particle density of states (DOS). At $T = 1.034T_c$, the data do not resemble the paramagnetic DOS of Fe as calculated in the disordered-local-moment limit.

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A long-standing question concerns the microscopic nature of the ferromagnetic to paramagnetic phase transition of the 3d-transition metals: Fe, Co, and Ni. Although there is no doubt that the long-range ferromagnetic order ceases to exist above the Curie temperature, T_c, it is a problem to reconcile this in a microscopic theory. There are several prominent models for explaining the loss of spontaneous magnetization upon heating to T_c: the Stoner Model,[1] the Disordered-Local-Moment picture (DLM)[2,3] and a model, based on disordering of some sort of magnetic clusters of size 10-30 Å, which is commonly referred to as the "Fluctuating Band" picture.[4] Also, spin-spiral configurations have been used for modeling the magnetic structure above T_c.[5]

In the Stoner model, the thermal effects enter only by the Fermi distribution[1] resulting in a T_c which is much too high[6] ("Stoner T_c"). The Stoner model has been improved[7] (called here the modified-Stoner model) by incorporating other temperature effects such as electron-phonon and spin-phonon coupling, into a function which is used to broaden the paramagnetic density of states (DOS). This, among other improvements, yields a more reasonable Curie temperature.

In the DLM model, magnetic moments are assumed to exist on the lattice sites which, above T_c, are assumed to be randomly distributed without short range order. Within this framework, the electronic structure has recently been calculated self-consistently by Pindor et al.[2] and Oguchi et al.[3] and, again, reasonable Curie temperatures have been obtained. It turned out that, for Fe, the magnetic moments vanished only at the very high Stoner T_c.

As a generalization of the DLM model, a new parametrized cluster theory is now available,[8] which allows calculation of the electronic structure for an arbitrary degree of short-range order. By comparison with spin-resolved photoemission data on Fe(100), a lower limit (4 Å) for the correlation length has been determined recently. It was noted that, for determining an upper limit, more experimental data are required.

The electronic structure of specific Fe valence band states at low temperatures has been studied by electron spectroscopic methods, such as photoemission,[9,10] and spin-resolved photoemission.[11] Good agreement with calculated band energies has been found. With increasing temperature, a slight reduction of the exchange splitting has been inferred from the photoemission data.[9,10] The spin-resolved measurements[11] revealed details on the wave-vector-dependent rebalancing of the spins with increasing temperature. The observation of "forbidden" peaks in the spin-resolved energy distribution curves (EDC's) at the binding energies of the states of opposite spin was taken as evidence for short-range correlations between neighboring magnetic moments.[8] "Collapsing" and "non-collapsing" states above E_F (exhibiting a vanishing or a nonvanishing exchange splitting above T_c, respectively, depending on the wave-vector) have been found with spin-polarized inverse photoemission.[12] In a temperature dependent x-ray photoelectron spectroscopy (XPS) study,[13] "no" changes were found with increasing temperature, but the actual data was not presented.

Any theory on the electronic structure has to be tested finally by its predicted DOS. Angle-resolved photoemission has been developed to a high degree of performance to test states as differentially as possible, but an integration to yield the DOS appears to be impossible. The only known method to test the DOS is valence-band XPS. Due to the high photon energies involved (> 1000 eV), information on the initial state k-vector is largely washed out.[15−18] As with any spectroscopic method, one has to be aware of the fact that the measurement might disturb the system, resulting in some distortion from the one-particle electronic structure. However, it will be seen from data taken at low (room) temperature with a clean surface that effects which are beyond the one-particle picture must be small for Fe. This is somewhat contrary to the case of Ni, where the observation of the 6 eV satellite and of the reduced valence band width[19] obscures the quantitative interpretation of XPS data in terms of the one-particle DOS.

It appears therefore that reliable valence band XPS data from Fe are desirable to determine the DOS above T_c and to compare with already existing

DOS calculations. We refer here specifically to predictions of the DOS above T_c in the DLM[2,3] picture and in the modified-Stoner[7] model mentioned earlier. The appearance of the calculated DOS above T_c is very different from that at $T = 0$. This change, if present, should be detectable by conventional valence band XPS. We have, therefore, performed XPS measurements on a well-characterized Fe(100) surface. A single-crystal was chosen rather than a polycrystal to ensure well-defined experimental conditions for ease of comparison with future valence-band XPS calculations, similar to those performed recently for alloys.[18]

The Fe(100) sample was cleaned in-situ by repeated cycles of argon-ion sputtering and heating. To avoid possible deflection of the emitted photoelectrons, the sample was demagnetized by heating above the Curie temperature (1043 K) prior to the XPS experiments. Separate test measurements[20] ensured that non-intrinsic temperature effects (e.g., a possible deflection of the beam due to the heating current) did not disturb the spectra taken at high temperatures. Surface cleanliness was checked by Auger spectroscopy. Prior to the measurements at room temperature, the contamination levels (corrected for Auger elemental sensitivity) were S/Fe = 0.03, C/Fe = 0.08 and N/Fe = 0.04.

Because of the surface sensitivity of the XPS method (it is, however, not really a surface specific method due to the escape depths of about 20 Å), a compromise had to be chosen between statistics (measuring time) and surface cleanliness in the high-temperature runs. The measuring times were chosen to obtain a small enough statistical error to enable to test for the predicted changes with temperature. During the runs, the S/Fe concentration increased to values between 0.065 and 0.214. No significant dependence of the XPS EDC on S concentration was observed in this range of surface contamination. This appears to be reasonable in view of the value of the escape depth.

The photon source used was unmonochromatized Mg K_α radiation (hν = 1253.6 eV). The zero of the binding energy scale was set to the Fermi edge of sputter-cleaned Pd. Data were taken in the multipass-average mode. The

angles of the source and analyzer with respect to the sample normal were 18.5° and 15°, respectively. The angular acceptance cone of the analyzer was ±6°. The EDC's at any temperature are normalized to the photon flux to detect relative temperature-induced intensity changes which had been an important issue in recent spin-resolved studies of Fe at elevated temperature.[11] Further experimental details will be presented elsewhere.[20]

Figure 1(a) shows the measured valence band XPS EDC of Fe at room temperature. The features are: a large peak approximately 1 eV below the Fermi energy E_F; a second peak which is smeared out to a shoulder around 3.3 eV binding energy; and a small feature at 4.5-5.5 eV. The position of these features is in gross agreement with previous room temperature measurements on Fe.[14,15,21] As compared to existing data on valence band XPS of Fe, the presented data appear to be the most reliable ones (in Refs. 14 and 15 difficult to control evaporated films have been used, and in Ref. 21 it is not clear whether the data had been obtained from Fe or FeS).

Remarkably, a "rigorous" calculation of the XPS energy distribution is not yet available for 3d-transition-metals. Therefore, the data, Fig. 1(a), is compared with the ferromagnetic spin-summed $T = 0$ DOS of Moruzzi, Janak and Williams[22] [see Fig. 1(b)], broadened only with what we know exactly: the instrument resolution function [composed of the Mg x-ray lineshape and the analyzer slit-width dependent resolution, which was 0.8 eV FWHM for the experimental data Figs. 1(a) and 2(e), and 1.0 eV FWHM for Figs. 2(a-d)]. There is good correlation between the positions of the features at 1, 3 and 5 eV in the theoretical and experimental DOS's of Fig. 1 where the 5 eV feature, although not very prominent in the data, is reproducible. The DOS and the experimental data are dissimilar in the relative intensity ratio of the low-energy shoulders to the leading peak. However, it is known that 3d matrix element effects tend to decrease the structures at higher binding energies relative to those near E_F by as much as 30% across the DOS.[23] This appears to yield better agreement also in the intensity ratios. Lifetime effects could be present on the order of the experimental

resolution but not significantly more. It has been found that fitting the data with the energy-dependent widths as observed in the ultraviolet photoemission experiments[9-11] smears out the weak structure at 5 eV binding energy. The observation of the broad photoemission lines[9-11] in Fe is therefore still a puzzle. These effects, as well as an electron-energy-loss background, are not (because of their quantitative uncertainties) included in the convolved DOS of Fig. 1(b). But they all tend to bring the relative peak heights into better agreement with the calculated DOS. We emphasize especially that there is no evidence for a valence band satellite in Fe as it has been inferred to exist from earlier valence band XPS data[14] and from more recent UPS photoemission data.[24]
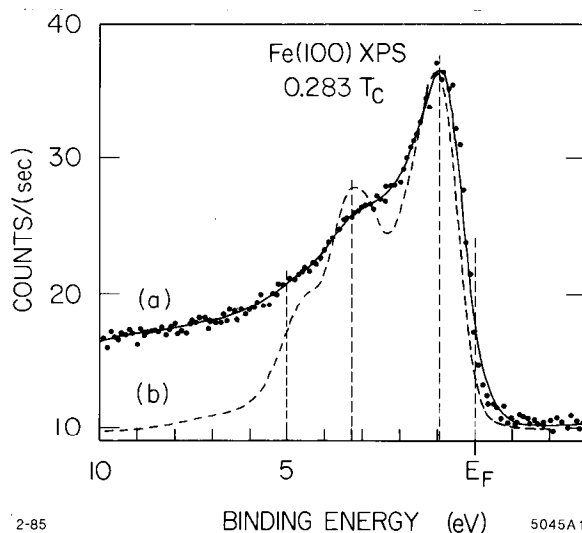

Fig. 1. (a) Experimental valence band XPS EDC of Fe at room temperature (...), with averaging spline fit (——); (b) theoretical Fe $T = 0$ DOS (after Moruzzi, Janak and Williams[22]), convolved with an instrument resolution of 0.8 eV FWHM (– – –). DOS is scaled to match intensity of the 1 eV peak.

A series of XPS EDC's taken at elevated temperatures up to $T = 1.034 T_c$ is shown in Figs. 2(a-e). As discussed above, in order to minimize sulfur segre-

gation, the data collection time was kept much shorter than that for the room temperature data [Fig. 1(a)], with a resulting loss of statistical accuracy. For ease of comparison, the data was fitted by an averaging spline-fitting routine.
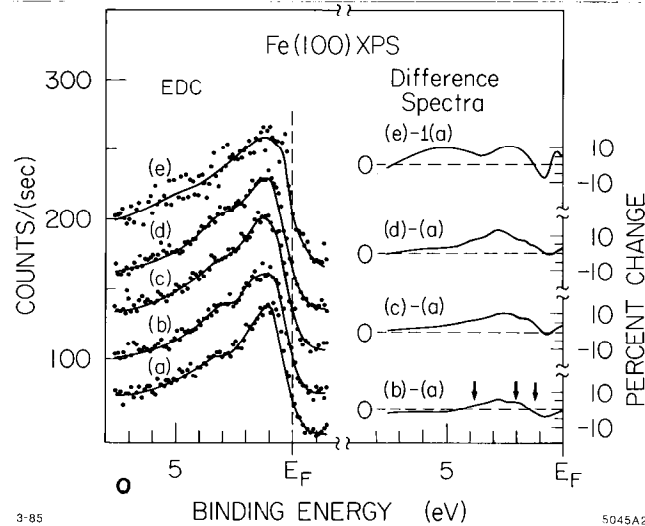

Fig. 2. (a-e) Experimental valence band XPS EDC's of Fe(100) at different temperature [1.0 eV instrument resolution in (a) to (d) and 0.8 eV in (e)]. (a) 0.283 T_c, (b) 0.860T_c, (c) 0.931 T_c, (d) 0.964 T_c, (e) 1.034 T_c. (b-d) displaced vertically for clarity by 30 counts/sec, (e) is 0.8 eV resolution data properly scaled and displaced 50 counts/sec. The difference spectra are determined using the appropriate room temperature curves [2(a) for b,c,d and 1(a) for e]. Indicated by arrows are the binding energies where the spin polarization of the theoretical $T = 0$ DOS is zero.

It is seen that the EDC's show slight monotonic changes with increasing temperature, the leading peak becoming reduced relatively to the hump near 3 eV. In Fig. 2, we also display the difference spectra of the EDC's taken at elevated temperatures against the appropriate room temperature curves of Figs. 1(a) and 2(a). In the difference curves, with increasing temperature we observe an increase

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in intensity at E_F and slightly above E_F (not shown) and an intensity decrease slightly below E_F, which can partially be attributed to the temperature smearing of the Fermi distribution.

We now compare the data with existing theories on the high temperature DOS of Fe. Figure 3 shows calculated DOS's from four references. The first is at $T = 0$ by Moruzzi et al.[22] (for comparison), while the remaining three at $T > T_c$ are: the modified Stoner (broadened paramagnetic) by Jarlborg and Peter,[7] the DLM by Pindor et al.[2] and the DLM by Oguchi et al.[3] The DLM calculations[2,3] showed that, although the magnetic moment did not change significantly up to T_c, the DOS differs appreciably from that at low temperatures. All are convolved with the 1.0 eV instrument resolution function for comparison with the EDC data of Fig. 2. It is seen that a strong decrease of the major peak in the DLM DOS's is predicted to occur at about 1 eV binding energy for Fe above T_c. The paramagnetic DOS (modified-Stoner model) of Jarlborg and Peter[7] has a largely reduced peak at about 0.5 eV as compared to the peak at 2.2 eV binding energy. All the high-temperature DOS calculations of Fig. 3 predict a decrease of the major peak of roughly 30% at around 1 eV binding energy. They also differ strongly in shape from the $T = 0$ curve. This remains so when comparing with the DLM DOS calculated using an enlarged lattice constant to take into account the thermal expansion (see Fig. 6 of Ref. 2).

When comparing the high-temperature experimental data (Fig. 2) with the theoretical DOS's (Fig. 3), it is apparent that the actual change in shape is much less than predicted, i.e. the major peak in the EDC is at about 1 eV below E_F, even above T_c. The difference curve for data above T_c (and separate fast temperature ramps monitoring the intensity at 1 eV binding energy[20]) shows about 10% decrease in amplitude near 1 eV while the intensity of the hump at 3 eV increases by about 10%.

In the spin-resolved photoemission study[11] on Fe(100) it was found that the photoemission intensity changes much less with temperature at that binding en-
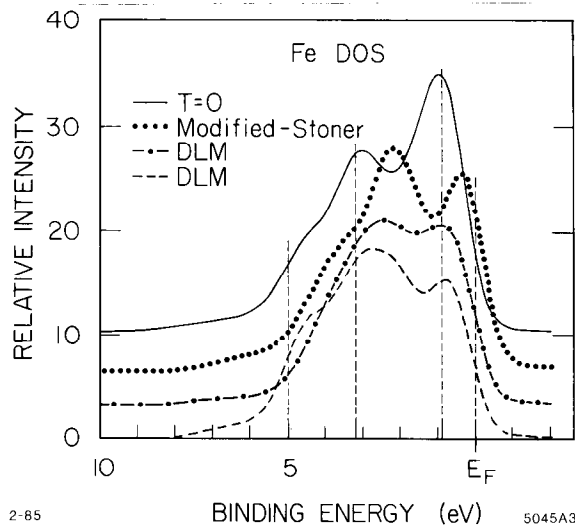
Fig. 3. Calculated DOS, each convolved with
1 eV instrument resolution. $T > T_c$: DLM (- - -
Ref. 2) (— · — Ref. 3); Modified-Stoner model (...
Ref. 7). $T = 0$ DOS (——— Ref. 22) included for
comparison. Curves displaced successively 3.3
units vertically for clarity.

ergy where the spin polarization is zero ("invariant point") than at other binding
energies. It had been pointed out also[25] that a similar effect might be present in
spin-resolved data on Ni. It is, therefore, interesting to analyze the present data
along this line, although certainly better statistics are desirable for this analysis.
The invariant points would be seen as zero crossings in the difference curves be-
tween high-temperature and the room temperature EDC's. We have indicated
in Fig. 2 on top of the $T = 0.860T_c$ difference curve, [(b)-(a)], by arrows the
binding energies where the spin polarization of the calculated DOS[22] is zero.
Certainly, there is some correlation in this data (the inflection near 2 eV bind-
ing energy might be a nonresolved zero crossing and at higher temperatures an
increasing background might raise the intensity at larger binding energies). We
are, however, aware of the fact that better statistics are needed (and future spin-
resolved XPS measurements) to show if such a correlation actually exists. These
remarks may stimulate further investigations using advanced light sources such

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as undulators to obtain better statistics since no theory presently accounts for a correlation between spin polarization and intensity changes with temperature.

In conclusion, high-temperature valence band XPS data on a controlled surface of Fe(100) are presented here for the first time. The data disagree with any of the previously predicted DOS's for Fe above T_c. The data show that the leading peak of the DOS becomes reduced, but much less than predicted. Very recent calculations yield agreement with the observed changes with a short-range order parameter of 5-6 Å.[26,27] It has been suggested by D. Pettifor (private communication) that the DLM predictions might be approached at temperatures far above T_c (but below the melting point) where the magnetic part of the specific heat vanishes. Studies are continued to test for this prediction.

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