Spin Polarization of Electrons Field Emitted from Single-Crystal Iron Surfaces

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The spin polarization of electrons field emitted from single-crystal iron surfaces was observed to be $(+25 \pm 5)\%$ for emission along [100], $(+20 \pm 5)\%$ along [111], and $(-5 \pm 10)\%$ along [110] (the polarization is positive for majority-spin electrons). These results correlate qualitatively with expectations from the bulk band model. However, quantitative calculations with bulk wave functions gave strongly parameter-dependent results. For meaningful calculations the effect of the surface on the wave functions must be included.

Measuring the electron-spin polarization (ESP) in emission from a solid in addition to energy and angular distribution is becoming a powerful tool in investigating the spin dependence of bulk and surface electronic structures.[1] The study of ferromagnetic $3d$ metals is especially of great interest since information can be gained on the range of validity of the one-electron band model and on the possible role of various many-body effects. To obtain such information it is crucial to work on single crystals since otherwise the directional dependence arising from the band structure will be averaged out, and even worse, this averaging will be affected in some unknown way because the work function varies along a polycrystalline surface. Among the $3d$ metals single-crystal ESP studies have so far been done only on Ni, using photoemission,[2] field emission,[3] and deuteron neutralization.[4] In this Letter we report on the first ESP data from well-defined single-crystal surfaces of iron. This iron study complements, in an important way, the Ni work because iron, unlike Ni, has both minority- and majority-spin d electrons at the Fermi level. The contribution of the latter is expected to influence the ESP and the comparison of the Ni and Fe results should provide additional information concerning the d states in ferromagnetic transition metals.

The electrons are extracted from the sample by field emission, which probes (in some approximation) the surface density of states directionally weighted perpendicular to the surface at the Fermi energy.[5,6] The technique we are using[7] is based on the field-emission microscope and allows us to select electrons for ESP measurements which have been emitted along well-defined crystallographic directions. The ESP is determined by means of a Mott detector.

Single-crystal iron emitters were obtained in the following manner: High-purity iron wire (99.99%) was drawn to 0.008 in. diameter and then electrolytically etched to form a tip. During the drawing sufficiently large crystallites are formed preferentially with the [110] direction parallel to the wire axis. As a consequence all the tips with small enough radii (<1000 Å) were [110]-oriented single-crystal emitters. Iron is chemically very reactive and therefore very difficult to clean. Brucker and Rhodin[8] found in their very careful studies of chemisorption on Fe(100) surfaces that iron cannot be cleaned by sputtering-annealing cycles since carbon is not removed in the process. Similarly we were unsuccessful in cleaning iron tips by means of dc UHV field desorption at low temperature ($\sim 80°K$). This always results in a characteristic final pattern observed in field emission which clearly indicates the presence of adsorbate(s). We conclude that in a positive electric field iron is desorbed whereas some adsorbate (which we guess to be carbon) stays at the iron surface and accumulates there during field desorption. This can be avoided by using H_2 promotion[9] in field desorption. Starting with a base pressure of 1×10^{-10} Torr we admitted 3×10^{-10}-Torr H_2 ($5.5N$ assayed grade) to the UHV system for field desorption. The desorption was monitored by observing the field-ion image on the fluorescent screen. It was possible to detect reproducible field-ion patterns after sufficiently long desorbing, even though the intensity was too low to obtain photographs. After desorption the H_2 was pumped to 1×10^{-9} Torr within 2 h and subsequently the chemisorbed hydrogen was removed from the tip with a short UHV field desorption. We note that only about one out of ten tips could be cleaned successfully because the tip radius in most cases became too large during desorption, and the results reported below have been obtained from four clean samples. The tips were kept at $\sim 80°K$ during cleaning and measuring. Figure 1 shows
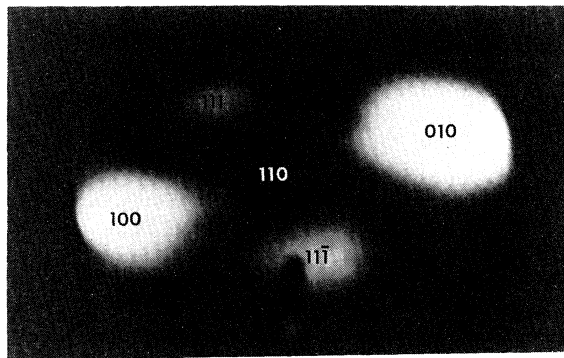
FIG. 1. Field-emission pattern of a [110]-oriented iron emitter, observed at an angle of ~40° from the screen. A portion of the (11$\bar{1}$) face is shaded out by the mirror support.

a field-emission pattern of a clean [110]-oriented iron tip. In the bcc symmetry the (100) and (111) planes are bright, and ESP data along these directions could be obtained within 10 min after the cleaning. The close-packed (110) face, on the other hand, is dark, the current density is extremely low, and therefore we can report only preliminary ESP data along [110].

The measurements were carried out in a magnetic field of 2.2 kOe parallel to the tip axis after saturating the sample in 12 kOe. No change of polarization could be observed when varying the magnetic field between 1.4 and 3.5 kOe.

For the ESP of field-emitted electrons from ferromagnetic iron we found $(+25 \pm 5)\%$ along [100], $(+20 \pm 5)\%$ along [110], and $(-5 \pm 10)\%$ along [110]. For not clean emitters the ESP was always found to be zero, and the given uncertainties represent estimated systematic errors. The positive sign means that majority-spin electrons are predominant in the current. These novel results yield direct information on the spin-dependent surface electronic structure in the vicinity of E_F. As a first step in the interpretation of these data, however, we start from the bulk band structure. There is no justification for this aside from the fact that bulk bands are available and that we wanted to see how close to experiment this simplest approach would take us. Self-consistent calculations of surface electronic structures of transition metals[10] are only now appearing in the literature and for the surface of ferromagnetic iron[11] in particular only one parametrized calculation is available at present.

The most recent and thorough *ab initio* calculation of the bulk band structure of iron is by Cal-

laway and Wang.[12] We derive from it that the ESP is $+100\%$ for field emission along [100]. This is because for the field strengths commonly used only Δ_1 states contribute to the field-emission current, and only the majority-spin Δ_1 band cuts E_F. We note that the surface calculation of Dempsey, Kleinman, and Caruthers[11] exhibits both majority- and minority-spin Δ_1 states at E_F in the center of the surface Brillouin zone at (100). This would reduce the expected ESP value and indicates that the discrepancy between experiment and band-structure value is in part a surface effect. Along [111] and [110], on the other hand, both majority- and minority-spin (bulk) bands which are strongly hybridized s-p (or plane wave) and d states contribute to the current. The tunneling probability for plane waves is believed to be 10–100 times larger than for d orbitals.[13,14] If we assume this to be true and therefore include only the plane-wave contribution to the current, we find an ESP of $+99\%$ along [111] and $+3.5\%$ along [110].[15] The trend in these values concurs with the experimental fact that the ESP is positive and substantial along [111] but small along [110]. However, the d-state current must be included in the calculation, especially for the [111] direction whose states are over 80% d.

It is straightforward to generalize the wave-matching calculation of Politzer and Cutler[14] to the case of hybridized bands: The plane-wave component in the wave function simply adds to the uniform component of the d wave over the matching plane (m.p.) and equations very similar to those following Eq. (32) in Ref. 14c are obtained. We then follow established practice and take the distance d of the m.p. from the last atomic layer to be about $\frac{1}{2}$ of the interlayer separation for that particular surface. For the (111) surface of bcc iron which has a lattice constant $a = 2.86$ Å, one-half of the interlayer separation is $D = a\sqrt{3}/12 = 0.413$ Å $= 0.78$ a.u. The iron $3d$ orbitals calculated by Herman and Skillman reach their maximum at ~0.4 a.u. Thus the value of the d orbital is not small at the m.p. As a result, the normal derivative at the m.p. (G_5 in the notation of Ref. 14c) for the Y_{20} orbital (which is of interest here) is large, rapidly varying with d, and of such a sign that the sign of the logarithmic derivative of the d wave at the m.p. is opposite to that of the plane-wave part in the wave function. This sign difference is a general feature of the Λ_1, Δ_1, or Σ_1 states at the Fermi surface of the transition metals because they are "antibonding"; the bonding s-d states are at the bottom of the d band.

Now, the value of the wave function at the m.p. must reflect the total normal derivative on the metal side of the m.p. because the logarithmic derivative on the vacuum side is fixed by the value of the work function. Because of the large value of G_5 and of the opposing signs, the calculated value of the field-emitted current turns out to be so sensitive to the position of the m.p. that it cannot provide a theoretical check on the experiment. The situation for the [110] direction is not so critical because the interlayer distance is large (3.8 a.u.), the d orbital is small at the m.p., and it does not change the order of magnitude of the field-emitted current from what we calculated for the plane wave alone.

In summary, we find that the method of the m.p. does not provide a means of calculating the dependence of the ESP on crystallographic direction, except in cases where the interlayer distance is large and the hybridization small, as is the case for Ni(100).[14] We conclude that, for a proper calculation, it is necessary to include explicitly the effect of the surface potential on the wave function and to calculate the latter far enough into the vacuum region such that they have reached their asymptotic decay rate. At this point the field-emitted current can be calculated by the standard method of the transfer Hamiltonian.[16]

To conclude, the present measurements on iron have shown striking differences in ESP for different high-symmetry crystallographic faces. Although the values of the ESP correlate qualitatively with what one expects from the bulk band structure, attempts to calculate the ESP more quantitatively using the matching-plane method are found to fail. The transfer Hamiltonian method, ultimately in conjunction with a full ferromagnetic surface calculation, is capable of giving accurate results for the ESP and will permit us to assess the importance of many-body effects. Such a test was, in fact, the chief motivation of the present measurements, and we hope that our results will stimulate such calculations for transition metals.

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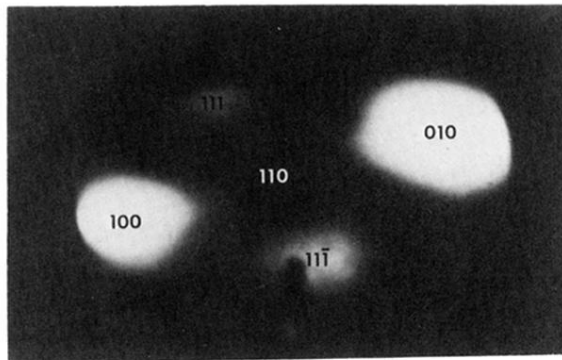
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