Evidence for the High-Spin to Low-Spin State Transition in Ordered Fe_3Pt Invar

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The electronic structure of ordered Fe_3Pt Invar has been studied by spin- and angle-resolved photoemission with synchrotron radiation as a function of temperature between $T/T_C=0.58$ and 1.3. An anomalous shift of photoemission intensities in the vicinity of E_F is found to accompany the ferromagnetic phase transition. This is interpreted semiquantitatively as resulting from the predicted changes in the electronic structure of *fcc Fe* occurring with the high-spin to low-spin state transition.

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For a long time it was thought that the Invar effect has its origin in a certain magnetic inhomogeneity of the systems since in most of the Invar alloys the anomalies are observed in a concentration range which is close to the fcc-bcc phase boundary, where the magnetic moment deviates downwards from the Slater-Pauling curve. This led Weiss[1] to his two-γ-state hypothesis, assuming that *fcc Fe* can exist in two distinct states, a low-spin state γ_1, which is antiferromagnetic and has a small volume ($a=3.57$ Å) and a small magnetic moment ($\mu=0.5\mu_B$), and a high-spin state γ_2 which is ferromagnetic and has a large atomic volume ($a=3.64$ Å) and a large moment ($\mu=2.8\mu_B$). For FeNi alloys, Weiss assumed the energy difference between these states to be a function of the Ni concentration, so that in the Invar regime ($Fe_{65}Ni_{35}$) γ_2 became the ground state and the antiferromagnetic γ_1 state became the excited state. Transitions from γ_2 to γ_1 with rising temperature then logically explained the Invar effect, since the expansion of the lattice with increasing T is compensated by a growing population of the low-volume γ_1 state.

The validity of the Weiss model, however, came into doubt when it was discovered[2] that fcc Fe_3Pt in the ordered state showed magnetovolume and thermal expansion anomalies similar to those of $Fe_{65}Ni_{35}$, yet with no deviation from the Slater-Pauling curve, and no signs for magnetic inhomogeneity. It was thus believed for some time that there might be two types of Invar systems, the large group of magnetically weak systems like FeNi, and the strong ferromagnets like Fe_3Pt or Fe_3Pd.[3]

New evidence for the correctness of the assumptions by Weiss came from band-structure calculations for pure Fe by Andersen *et al.*[4] and by Kübler,[5] which showed that (at $T=0$) in the fcc state a rapid transition from an antiferromagnetic ground state with low moment ($\mu=0.55\mu_B$) to a ferromagnetic state with high moment ($\mu=2.32\mu_B$) ($\Delta E=0.3$ eV) occurs within a narrow range in which the radius r_s of the Wigner-Seitz cell changes from $r_s=2.54$ a.u. to $r_s=2.65$ a.u. Recent band-structure calculations by different authors confirm these results.[6-9]

In a previous investigation of the electronic properties of ordered Fe_3Pt we have shown that spin-resolved energy distribution curves taken at room temperature and slightly below exhibit the spin-split electronic structure of the alloy with an exchange splitting near the X point of 2.1 ± 0.2 eV.[10] This value and the position of the spin-resolved peaks were found to agree reasonably well with a recent band-structure calculation by Hasegawa.[11]

The crystal structure of ordered Fe_3Pt is fcc with the Fe atoms occupying the face centers and the Pt atoms the corners of the unit cell. Because of the dominance of the Fe in the chemical composition, a close relation to the electronic properties of *pure fcc* Fe is to be expected. Indeed, we have shown previously[10] that the energy bands of ordered $Fe_3Pt(001)$ at low temperatures closely resemble those of pure fcc Fe[6] in the high-spin state, if the different forms and sizes of the reciprocal lattices (bcc for fcc Fe and simple cubic for ordered Fe_3Pt) are taken into account. Therefore, it is possible in this work for the first time to test the prediction of Weiss[1] that the origin of the Invar effect is the high-spin to low-spin state transition of fcc Fe, by studying the temperature dependence of the photoemission spectra of Fe_3Pt and comparing it with the respective band structures of fcc Fe.

The experiment has been conducted at the beam line TGM1 of the Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung (BESSY) storage ring in West Berlin, Germany. We made use of the spin-resolving photoelectron spectrometer as described elsewhere.[12] The energy resolution was 0.4 eV, and the angular resolution $\pm3°$. The Fermi energy was determined within ±0.05 eV by comparison with data taken from a Ag target. The sample could be radiatively heated by a bifilar-wound tungsten filament and could also be cooled to about $-25\,°C$. A single crystal with analyzed composition $Fe_{72}Pt_{28}$ has been grown by the Bridgman technique in an Al_2O_3 crucible in 740-Torr Ar atmosphere. The frame-shaped sample cut from the crystal in an (100) plane had been annealed and cooled at a rate of $20\,°C/d$ from $870\,°C$ to $500\,°C$ to install the long-range order. The sample was cleaned *in situ* by repeated ion etching and heating cycles. It was found necessary to

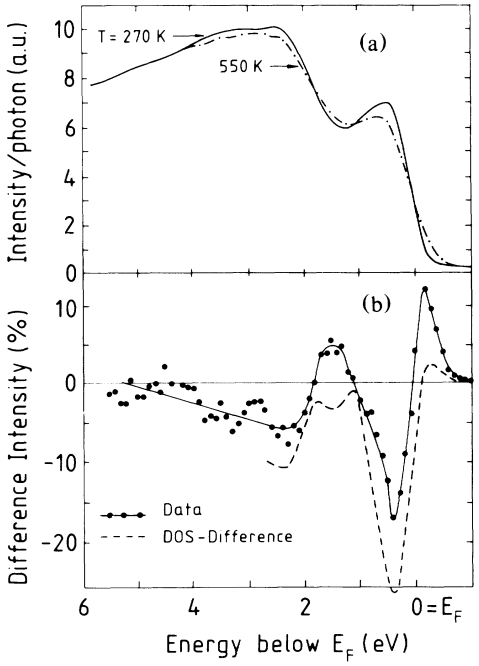

FIG. 1. (a) Angle-resolved energy distribution curves from $Fe_3Pt(001)$ for normal emission and s-polarized light at 60 eV photon energy at 270 and 550 K ($T_C = 450$ K). The intensities are normalized to the photon flux. (b) Difference between EDC's taken at 550 and 270 K. The dashed line is the difference between the fcc Fe DOS's at $a = 3.71$ Å (high-spin state) and $a = 3.46$ Å (low-spin state) (see Ref. 6), convoluted with a 0.4-eV-FWHM Gaussian-type resolution function after truncation by the temperature-dependent Fermi function.

heat the sample up to 770 °C to obtain a high spin polarization. Cleanliness was checked by Auger electron spectroscopy. After flashing, only minor residual C and S contaminations have been found.

In Fig. 1(a), we display angle-resolved electron distribution curves (EDC's) taken at 60 eV photon energy for normal emission and normal-incident light at 270 K ($T/T_C = 0.6$) and at 550 K ($T/T_C = 1.22$, $T_C = 450$ K). At $T = 270$ K, the shape of the Fermi-energy cutoff is determined mainly by the experimental resolution. Spin-resolved data[10] show that the peak at 0.4 eV binding energy consists of majority-spin and minority-spin intensities. The (dominating) minority-spin contribution has been attributed to the $\Delta_5^{\downarrow}$ band along the Γ-X direction, whereas the majority-spin contribution is attributed to emission from a very flat band of $\Delta_2^{\uparrow}$ symmetry which is predicted to be at 0.1 eV below E_F [cf. Fig. 2(a)]. The peak at 2.5 eV binding energy (E_B) is due to the $\Delta_5^{\uparrow}$ band, and the $\Delta_5^{\uparrow,\downarrow}$ exchange splitting is 2.1 ± 0.2 eV.[10]

As seen in Fig. 1(a), data taken above T_C differ from the low-temperature data by a significant *decrease* in intensity in the vicinity of $E_B = 0.4$ eV and an *increase* in intensity within an energy range of about 0.5 eV above

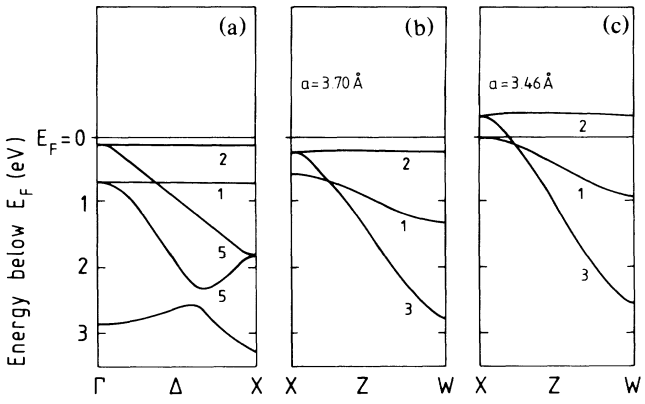

FIG. 2. (a) The majority-spin band structure of Fe_3Pt along Γ-X (Ref. 11). (b) The majority-spin band structure of fcc Fe along X-W in the high-spin state ($a = 3.71$ Å) (see Ref. 6). (c) As in (b), but for the low-spin state.

E_F. At E_F, the intensity does not change with temperature. This is the case for EDC's at any temperature which has been studied [at $T/T_C = 0.6$, 0.7, 1, and 1.22, only two of which are shown in Fig. 1(a)]. In Fig. 1(b), we show the difference curve between the EDC's taken at $T = 270$ and $T = 550$ K (full line and dots). The difference curve exhibits a characteristic pattern, with a peak at 0.1 eV above E_F, a minimum at 0.4 eV below E_F, and a broad maximum near $E_B = 1.5$ eV.

The photoemission intensity $I(E)$ at a given temperature is proportional to $F(E,T)D(E)$, where $F(E,T)$ is the Fermi function and $D(E)$ is the symmetry-projected density of states (DOS). For comparison with the experimental data, $I(E)$ has to be convoluted with the apparatus resolution function. The increase in intensity above E_F is an order of magnitude larger than expected from the variation of the Fermi function with temperature alone. We conclude therefore that $D(E)$ also depends on temperature in the vicinity of E_F and that a certain electronic state at binding energy some tenths of an electronvolt *below* E_F for $T < T_C$ shifts towards an energy slightly *above* E_F when the temperature is raised to $T > T_C$.

To obtain an indication for the decrease of the spontaneous magnetization with temperature which accompanies the ferromagnetic phase transition of the specific sample under investigation, we display in Fig. 3 the measured temperature dependence of the secondary-electron spin polarization near zero kinetic energy. Also shown in Fig. 3 is the integrated intensity above E_F [cf. Fig. 1(a)] in EDC's taken at different temperatures. One can see that in the range close to T_C the decrease in polarization is accompanied by a steplike increase in the integrated intensity above E_F. This suggests that this change is related to the magnetic phase transition in Fe_3Pt around T_C, i.e., to the transition from the ferromagnetic ground

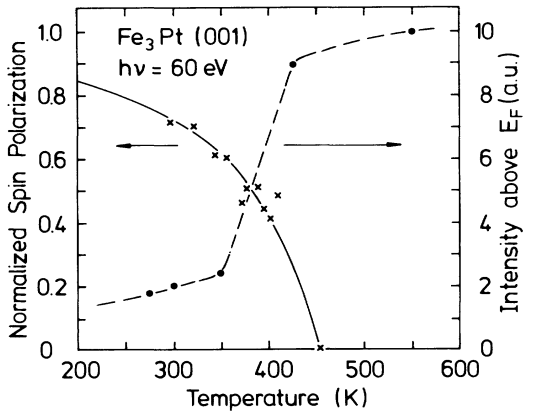

FIG. 3. Normalized secondary-electron spin polarization and integrated angle-resolved photoemission intensity above E_F from Fe_3Pt as functions of temperature.

state γ_2 to the antiferromagnetic (or nonmagnetic) excited state γ_1.

No calculation on the changes in the electronic structure of Fe_3Pt or any other Invar alloy with temperature is yet available. Therefore, we try to interpret the data on the basis of Weiss's hypothesis, making use of the similarity in the electronic structures of Fe_3Pt and of fcc Fe.[10] The fcc Fe band structure has been calculated as a function of the lattice constant a by Bagayoko and Callaway.[6] They predict that fcc Fe has a large magnetic moment (high-spin state) at a lattice constant larger than 3.63 Å and a small magnetic moment (low-spin state) at smaller lattice constants. This is largely due to the dependence of the binding energy of a very flat majority-spin band with Z_2 symmetry (along X-W) on the lattice constant. This band is located at $E_B=0.26$ eV in the high-spin state ($a=3.71$ Å) and shifts rapidly through E_F with decreasing lattice constant [compare Figs. 2(b) and 2(c)], in correspondence to the smaller exchange splitting. The changes in the DOS of fcc Fe in the vicinity of E_F occurring with the high-spin to low-spin state transition are largely due to the shift of this flat majority-spin band of Z_2 symmetry.[6]

Since the crystal structures of Fe_3Pt and pure fcc Fe are similar, the Γ-X distance in the simple cubic reciprocal lattice of Fe_3Pt is $\frac{1}{2}$ of that of the corresponding distance in the bcc reciprocal lattice of fcc Fe. Therefore, bands of fcc Fe in the right part of the Γ-X direction are folded back towards Γ in Fe_3Pt, and bands along X-W add to those along Γ-X. The folded-band structures of fcc Fe in the high-spin state ($a=3.7$ Å) and Fe_3Pt ($a=3.75$ Å) are then indeed similar,[10] and the Z_2-symmetry band in fcc Fe located at $E_B=0.26$ eV corresponds to a similarly flat band in the Fe_3Pt along Γ-X of Δ_5 symmetry, with a calculated binding energy of 0.1 eV.[11] We have shown previously that this band contributes to part of the peak intensity near E_F in the EDC at $T=270$ K in Fig. 1.[10] Therefore, it is reasonable to compare in Fig. 1(b) the experimental EDC difference curve with the change in the DOS of fcc Fe predicted to accompany the high-spin to low-spin state transition. The dashed line in Fig. 1(b) represents the difference curve between the fcc Fe DOS's at $a=3.71$ Å (high-spin state) and at $a=3.46$ Å (low-spin state). Prior to performing the subtraction of the two DOS's, the effect of the Fermi function at the proper temperature has been taken into account, and the resulting DOS's have been convoluted with the experimental resolution function. A close similarity to the experimental EDC-difference curve is observed which suggests that both curves are of the same physical origin.

We conclude therefore that the observed changes in intensity in the vicinity of E_F in the EDC's of $Fe_3Pt(001)$ are mainly caused by the aforementioned shifting of the flat band through E_F with increasing temperature due to thermal excitation of the low-spin state. As suggested by Weiss,[1] the low-spin state in the Invar alloys is higher in energy than the high-spin state by less than 0.1 eV (depending on the Fe concentration) which makes it accessible by thermal excitation.

The peak above E_F in the experimental difference curve [cf. Fig. 1(b)] is not as large as it is in the DOS difference curve [cf. Fig. 1(b)]. Probably, the $X_2^\downarrow$ band does not shift to as high an energy as anticipated for the fcc Fe at the assumed lattice constant of 3.46 Å. Also, the changes occurring in the electronic structure of the Fe_3Pt alloy with increasing temperature might be somewhat different from those occurring in pure fcc Fe as a function of the lattice constant.

The amplitude of the intensity above E_F would be a measure of the weight of the low-spin state. It has been shown by Holden, Heine, and Samson[13] that the fractional change of the radius of the Wigner-Seitz cell, i.e., the fractional linear expansion, is related to the change of the local magnetic moment with temperature by

$$\frac{I(T_1)-I(T=0)}{I(T=0)} = a[U(T_1)-U(T=0)] + b[m^2(T_1)-m^2(T=0)], \quad (1)$$

where a and b are constants, U is the internal energy, and m is the value of the local moment at $T=0$ K and at an elevated temperature $T_1 \gtrsim T_C$. It was shown[13] that in the Invar alloys the m^2 term in Eq. (1) is, generally, dominant, and describes the observed decrease in length (or volume). Therefore, the fractional volume change should be proportional to m^2, which is proportional to the square of the intensity above E_F. We note that the square of the intensity above E_F (Fig. 3) follows qualitatively the temperature dependence of the fractional volume change of Fe_3Pt Invar.[14]

In conclusion, we have observed an anomalous change in photemission intensity from ordered $Fe_3Pt(001)$ in the vicinity of E_F which appears to be related to the

ferromagnetic-to-paramagnetic phase transition. The data can be interpreted semiquantitatively in terms of the changes in the electronic structure of *fcc* Fe predicted to accompany the high-spin to low-spin state phase transition as a function of the lattice constant.[6] This supports strongly the hypothesis of Weiss[1] that the Invar effect is related to the electronic properties of fcc Fe.

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