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Magnetic and transport properties of the itinerant electron system $\text{Hf}_{1-x}\text{Ta}_x\text{Fe}_2$

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Magnetization and resistivity measurements of poly- and single-crystalline samples of $\text{Hf}_{1-x}\text{Ta}_x\text{Fe}_2$ are presented. At the antiferromagnetic to ferromagnetic transition we find a large change of resistance which can be induced as a function of temperature as well as field. For single-crystalline $\text{Hf}_{0.86}\text{Ta}_{0.14}\text{Fe}_2$ we observe at room temperature a giant magnetoresistance effect of 6%. From neutron-powder-diffraction measurements, possible magnetic structures in the different magnetic states are constructed. © 1997 American Institute of Physics. [S0021-8979(97)27308-1]

I. INTRODUCTION

The pseudobinary system $\text{Hf}_{1-x}\text{Ta}_x\text{Fe}_2$ can be classified as an itinerant-electron magnet closely related to the HfFe_2 and TaFe_2 compounds which crystallize in the MgZn_2 -type Laves-phase structure.¹ The magnetic ground state changes from ferromagnetic (F) to antiferromagnetic (AF) at a tantalum content of about $x=0.3$. The samples with $x>0.1$ exhibit in addition to the low-temperature F state, also AF order at higher temperatures. Near $x=0.2$, a first-order magnetic phase transition from F to AF occurs with increasing temperature.² Moreover, for these compounds the AF to F transition temperature is influenced by an external field. At constant temperature, a magnetic field of typically a few Tesla can induce a metamagnetic transition, which is accompanied by a large change in resistance, a so-called giant magnetoresistance (GMR) effect. Here, we report on resistance and magnetization measurements on poly- and single-crystalline samples. Furthermore, neutron-powder-diffraction experiments have been performed to investigate the crystallographic and magnetic structure.

II. SAMPLE PREPARATION

Three polycrystalline $\text{Hf}_{1-x}\text{Ta}_x\text{Fe}_2$ samples with nominal tantalum contents of $x=0.15$, 0.20, and 0.25 were prepared by arc-melting the pure starting materials in a water-cooled copper crucible in a continuously titanium-gettered argon atmosphere. The purity of the starting materials is 99.9%. The samples were wrapped in tantalum foil and then annealed in water-free quartz ampoules at 1000 °C for one week under an argon atmosphere of 200 mbar. Chemical analysis revealed that the actual tantalum contents of the annealed samples are $x=0.17$, 0.21, and 0.26.

Furthermore, two single-crystalline samples were grown by the traveling-floating-zone method in an adapted NEC double-ellipsoidal-type image furnace. The feeds, with composition $\text{Hf}_{0.80}\text{Ta}_{0.20}\text{Fe}_{2.05}$ and $\text{Hf}_{0.86}\text{Ta}_{0.14}\text{Fe}_{2.05}$, had an excess of iron to compensate for evaporation of iron during growth. The crystals were grown under an argon atmosphere of 800 mbar with a speed of 8 mm/h. Laue x-ray photo-

graphs of the single crystals displayed sharp diffraction spots, indicating crystalline perfection. The actual composition obtained by chemical analysis of the single crystal with nominal composition $\text{Hf}_{0.80}\text{Ta}_{0.20}\text{Fe}_{2.05}$ was found to be $\text{Hf}_{0.78}\text{Ta}_{0.22}\text{Fe}_2$.

III. RESULTS AND DISCUSSION

Neutron-powder-diffractograms, taken with diffractometer E6 at the Hahn–Meitner Institute, Berlin, were collected at various temperatures in the paramagnetic (P), AF, and F state for the samples with $x=0.17$ and 0.21. For this purpose, polycrystalline samples with a mass of about 10 g were mounted in an orange-type cryofurnace. The incident wavelength used was 2.412 Å. The recorded spectra were analyzed by means of the Rietveld profile procedure,³ using the program FullProf.⁴ The neutron-powder-diffraction pattern of the sample with $x=0.21$ in the P state (Fig. 1, $T=400$ K) can be indexed with the MgZn_2 -type structure (space group $P6_3/mmc$). The small peaks at $2\theta=57^\circ$ and

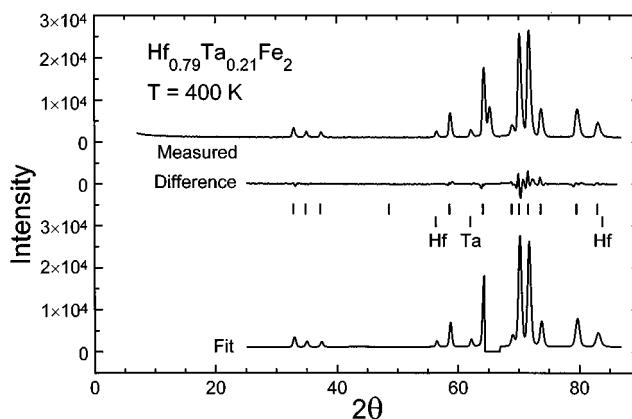


FIG. 1. Neutron-powder-diffraction data of $\text{Hf}_{0.79}\text{Ta}_{0.21}\text{Fe}_2$ taken at 400 K (P state). In the middle of the figure the difference is displayed between the measured spectrum (top) and the fit obtained in Rietveld refinement (bottom). All peaks could be identified to belong to either the bulk phase or to pure hafnium or tantalum. The peak at 66° is most probably due to the aluminum cryostat.

TABLE I. Lattice parameters of $\text{Hf}_{0.79}\text{Ta}_{0.21}\text{Fe}_2$ at three different temperatures obtained through Rietveld refinement of neutron-powder-diffraction spectra.

$\text{Hf}_{0.79}\text{Ta}_{0.21}\text{Fe}_2$	P state ($T=400$ K)	AF state ($T=200$ K)	F state ($T=50$ K)
a (Å)	4.929(1)	4.890(1)	4.922(1)
c (Å)	8.053(1)	7.992(2)	8.024(1)

62° are attributed to small amounts of pure hafnium and tantalum present in the sample. The volume fraction of both elements is estimated to be less than 1%.

In the MgZn_2 -type structure, iron occupies two different sites: the $2a$ site with position (0,0,0) and the $6h$ site with position $(1/2y, y, 0.25)$, while the hafnium or tantalum atoms occupy the $4f$ site $(0.33, 0.67, z)$. In this structure, the iron atoms are located in successive layers of $2a$ and $6h$ sites perpendicular to the c axis. In the unit cell are two layers of each kind. The values of y and z obtained in the Rietveld refinement are $y=1.661(1)$ and $z=0.0637(7)$. The lattice parameters in the three different magnetic states are given in Table I. The unit-cell volumes found are systematically smaller than reported in previous publications,^{2,5} which may be attributed to the absence of zirconium in our starting material.

From the difference in the spectra of the F and P state, we find evidence for magnetic contributions to several reflections, e.g., (100), (002), (101), and (202). The observation of magnetic scattering on reflection (002), indicates that the direction of the moment is not along the c axis, which is in contrast with the assumption made by Nishihara and Yamaguchi² to interpret their Mössbauer spectra. Refinement of the F spectrum under the assumption that the $2a$ and $6h$ iron moments have the same size and direction, suggests that the moments are directed in the basal plane and have a size of about $1\mu_B$.

In the AF state, no additional magnetic peaks are observed, which implies that the AF unit-cell is of the same size as the crystallographic unit cell. A possible magnetic unit cell based on our neutron-powder-diffraction results together with the Mössbauer data of Nishihara and Yamaguchi² is a TiFe_2 type of magnetic unit cell,⁶ in which the $6h$ planes are antiferromagnetically coupled, while the $2a$ atoms have no net magnetic moment due to frustration. The moments appear to be in the basal plane. However, the Rietveld refinement is not conclusive about this structure. The analysis of neutron-diffraction measurements on single crystals are on the way.

Magnetization measurements were performed in a SQUID magnetometer at temperatures between 5 and 350 K in magnetic fields up to 5 T. The AF–F transition occurs at 279 and 183 K for the $x=0.17$ and 0.21 samples, respectively. For the sample with $x=0.26$, no AF–F transition is observed. The AF–P transition is seen as a maximum in magnetization at about 340 K for all three samples. These results are in good agreement with the magnetic phase diagram of Nishihara and Yamaguchi.² The spontaneous magnetic moment at 5 K decreases with increasing tantalum con-

TABLE II. Compositional and magnetic information about $\text{Hf}_{1-x}\text{Ta}_x\text{Fe}_2$ compounds. The actual values of the tantalum content have been determined by chemical analysis. T_N and T_0 are the Néel temperature and the temperatures of the AF–F transition, respectively. μ_S is the spontaneous magnetic moment per iron atom at 5 K. $\Delta R/R$ is the change in resistance at the AF–F transition.

Nominal x	0.15	0.20	0.25	0.20 ^a	0.14 ^a
Actual x	0.17	0.21	0.26	0.22	...
T_N (K)	340	340	340	336	325
T_0 (K)	279	183	...	105	285
μ_S (μ_B/Fe)	1.16	1.04	...	$\parallel a$: 1.23 $\parallel c$: 1.13	...
$\Delta R/R$ (%)	12	35	...	37	6

^aSingle-crystalline sample.

centration. Magnetization measurements at 5 K on the single crystal with $x=0.22$ reveal the easy magnetization to be in the basal plane. The magnetizations measured with the field along the a and the c axis coincide at 3 T. The AF–F transition is observed at 105 K and has a temperature hysteresis of 15 K.

This transition temperature is 78 K lower than the transition temperature of the polycrystalline sample with an initial tantalum content of 0.20 (see Table II). The samples have been prepared by completely different methods, leading not only to differences in tantalum concentration, but possibly also resulting in differences in the iron content. Herbst *et al.*⁵ have reported that the AF–F transition temperature also depends on the iron content. The discrepancy in the observed values of the AF–F transition temperatures may be explained by variations in the actual composition of the compounds.

Magnetization curves measured at temperatures around the AF state of the single crystal with $x=0.14$ are displayed in Fig. 2. It should be noted that these curves show only very weak hysteresis, in contrast to the temperature dependence of the magnetization at the AF–F transition. The transition field is determined as the maximum of the first derivative of the magnetic isotherms. The thus obtained magnetic phase diagram is given in the inset of Fig. 2.

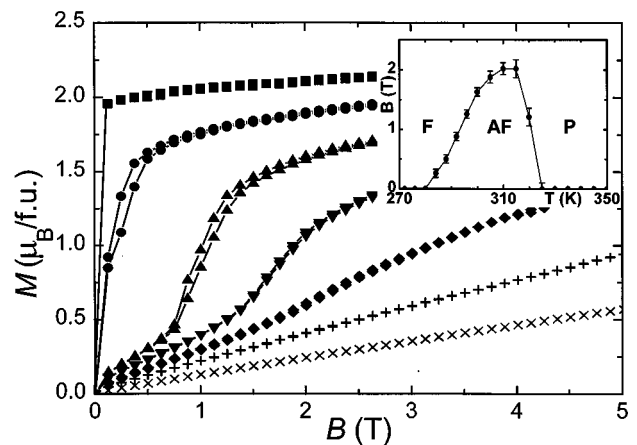


FIG. 2. Magnetization isotherms of $\text{Hf}_{0.86}\text{Ta}_{0.14}\text{Fe}_2$ at 272 K (■), 284 K (●), 292 K (▲), 300 K (▼), 310 K (◆), 325 K (+), and 350 K (×). The transition field is determined as the maximum of the first derivative of the magnetic isotherms. The resulting phase diagram is shown in the inset.

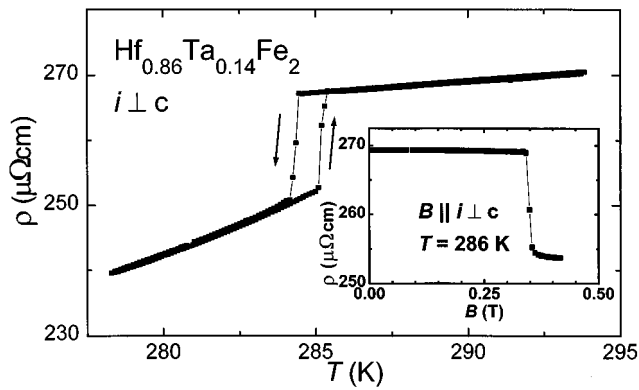


FIG. 3. Resistivity of single-crystalline $\text{Hf}_{0.86}\text{Ta}_{0.14}\text{Fe}_2$ for the current in the basal plane. In the inset, the magnetoresistance at 286 K for $B \parallel i \perp c$ is displayed.

The temperature and field dependence of the electrical resistivity were measured by a conventional ac-four-probe method. The samples were shaped by means of spark erosion into bars with dimensions $1 \times 1 \times 4 \text{ mm}^3$ suitable for electrical-resistivity measurements. Optical inspection of samples cut from polycrystalline ingots revealed microcracks, which make it impossible to give absolute resistivity values. Furthermore, it turned out that thermal cycling increases the number of cracks causing the resistance measurements performed with increasing and decreasing temperature to not coincide. Resistivity measurements made on single crystals did not show this difficulty. A possible explanation for the formation of the cracks is the very anisotropic thermal expansion,² which introduces stresses at the grain boundaries. In zero field, we find normal metallic behavior for all samples; however, the AF–F transition is accompanied by a drastic reduction of the resistivity (see Table II). With de-

creasing transition temperature the relative size of the resistance step increases. The temperature dependence of the resistivity near room temperature of the single crystal with $x=0.14$ is shown in Fig. 3. The strong reduction in resistivity can also be induced by an applied magnetic field, as depicted in the inset of Fig. 3. In both cases the change in resistance $(R_{AF}-R_F)/R_F$ amounts to 6%.

IV. SUMMARY

We have presented magnetization and resistivity measurements of poly- and single-crystalline samples of $\text{Hf}_{1-x}\text{Ta}_x\text{Fe}_2$. The magnetic transition temperatures are in good agreement with the magnetic phase diagram reported by Nishihara and Yamaguchi.² From Rietveld refinement of neutron-powder-diffraction spectra, we conclude that in the F state the moments of the iron atoms are aligned in the basal plane and have a value of about $1 \mu_B$. The AF unit cell is of the same size as the crystallographic unit cell. Rietveld refinement of the neutron-powder-diffraction spectra is not conclusive about the details of the magnetic structure. A possible magnetic structure is a TiFe_2 -type of structure.⁶ At the AF to F transition, we find a large change of resistance which can be induced as a function of temperature as well as field. For single-crystalline $\text{Hf}_{0.86}\text{Ta}_{0.14}\text{Fe}_2$, we have observed a GMR effect of 6% at room temperature.

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