"Double" Ferromagnetism in $Gd_{70}Y_{30}$ Single Crystals

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Magnetic-susceptibility, electrical-resistivity, and specific-heat measurements on $Gd_{70}Y_{30}$ single crystals show Curie-Weiss behavior down to a T_C of 218.8 K along both c and α axes. Below 218.8 K the α -axis sample shows a second (hence the term "double") Curie-Weiss behavior down to 205.5 K while the c -axis sample exhibits a constant magnetic moment. A model is proposed which places the Gd moments on a cone about the c axis at 218.8 K with the random basal-plane component ordering subsequently at 205.5 K.

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In a search for Lifshitz points among rareearth alloys we chanced upon a new magnetic ordering phenomenon in $Gd_{70}Y_{30}$ which we shall refer to as "double" ferromagnetism. The case unfolds as follows: In Fig. 1, we show vibratingsample magnetization data at 30 Oe for pure Gd single crystals; these data are helpful for understanding the alloy results. It is seen that for Gd the easy direction just below the 293 K ordering temperature is along the c axis. Then as the temperature is lowered the easy direction changes to the a direction near 230 K much like results prethe *a* direction hear zoo K much like results provided. $1 - 4$ In Fig. 2, we show similar magnetization data for $Gd_{66}Y_{34}$ which turns out to be antiferromagnetic between 166 and 206 K; this result is in agreement with previously reported observations.⁵⁻⁷

The surprising magnetization results are those for $Gd_{70}Y_{30}$ shown in Fig. 3. Here the magnetic moment grows with decreasing temperature in Curie-Weiss style for both a -axis and c -axis samples down to the T_c of 218.8 K. Then the concave-upward rise of the moment (in contrast to

FIG. 1. Constant-field magnetization vs temperature for Gd single crystals.

the concave-downward Gd data) along the a axis continues in a second Curie-Weiss fashion down to the second Curie temperature T_c^1 of 205.5 K. The two Curie-Weiss regimes encountered are suggestive of "double" ferromagnetism.

The observed drop in c -axis moment below 205. 5 K is attributed to the onset of twofold magnetic anisotropy as the easy direction goes to the basal plane. Further observations at stronger applied magnetic fields showed that the second ordering temperature could be eliminated. This was found to occur when the internal field exceeded 200 Oe.

A model which fits the results places the moments on the surface of a cone around the c axis at T_c (218.8 K) with the basal-plane component random down to T_{c} ¹ (205.5 K) below which simple ferromagnetism obtains.

This model would require specific-heat anomalies (peaks) at 205.5 and 218.8 K, and so we were motivated to obtain such data. We were

FIG. 2. Constant-field magnetization vs temperature for $Gd_{66}Y_{34}$ single crystals.

FIG. 3. Constant-field magnetization vs temperature for $Gd_{70}Y_{30}$ single crystals.

pleased to find the results shown in Fig. 4, where the magnetic peaks expected for the model are seen. This result may be readily used to eliminate an explanation of the data in terms of technical magnetization (Bloch walls, domains, etc.). For pure $Gd⁴$ there is only the peak at the Curie point with very little evidence of sizable specificheat effects related to technical magnetization or anisotropy effects.

Results of electrical resistivity measurements are shown in Fig. 5. Here the results are reminiscent of the data⁴ for Gd. No evidence for antiferromagnetism (Fermi-surface-area effects) are in evidence although a greatly enlarged plot (not shown) of the resistivity data made the magnetic transitions perceptible. These findings are such that the "double"-ferromagnetism model finds compatability here. It appears that "double" ferromagnetism occurs for yttrium concentra-

FIG. 5. Electrical resistivity vs temperature for $Gd_{70}Y_{30}$ single crystals.

tions in Gd between 12 and 30 at. %. Detailed results will be given in another paper which is being prepared.

Neutron diffraction experiments will be carried out to test further the validity of the proposed model.

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FIG. 4. Specific heat vs temperature for $Gd_{70}Y_{30}$.

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Characterization of the Hydrogen Adsorption/Absorption Process for Nb(110) with Surface Spectroscopy

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Angle-resolved photoemission studies of H on the Nb(110) surface show H-related structures with photon-energy —dependent binding energies in normal emission. The development of these features with H₂ exposure is pressure and energy dependent. These properties, together with a reversible temperature-dependent amplitude, are attributed to an initial adsorption regime followed by ab sorption of hydrogen into the near-surface substrate layers of Nb.

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The behavior of hydrogen on transition-metal surfaces has not been historically the simple problem that was anticipated by both experimentalists and theorists. Recently this has become evident through studies of the hydrogen-stabilized reconstruction of $W(001)$,¹ and the surface geometry of hydrogen chemisorbed on surfaces of Pd (Ref. 2) and Ti.³ For Pd+H at room temperature no hydrogen bonding orbital is seen in photoemission studies although subtle changes do occur in the vicinity of the d bands.⁴ Cooling the Pd sample results in observation of the ^H bonding orbital' and even permits a mapping of the two-dimensional band structure of the adlayer.⁶ The suggestion is made that the negative observation at room temperature is simply due to the fact that ^H moves into the bulk, i.e., out of the surface region probed by photoemission, as the sample is warmed up to room temperature. For Nb(110) $+$ H it was reported previously⁷ that a two-state chemisorption picture seemed appropriate although absorption into the subsurface region could not be ruled out completely. Because of the tendency for Nb to absorb H it seems appropriate to study the details of the sorption process. In particular it is important to determine precisely where the ^H atoms are located relative to the Nb surface layer if one wants to understand the electronic structure.

We have performed angle-resolved photoemission measurements for Nb(110) single-crystal surfaces and find results which suggest that at room temperature the hydrogen is not only adsorbed on the surface, but also absorbed into the near surface region. A saturation exposure to H is found to yield a three-dimensional $Nb + H$ complex, and the exposure required for saturation depends not only on temperature but also on pressure and on the *sampling depth* of the measurement. It is suggested that a multilayer extension of the thermodynamic picture used recently to exof the thermodynalific picture used recently to e
plain H-uptake experiments in Nb⁸ is needed for describing the near-surface distribution of H in Nb (110).

The experimental apparatus used here has been described previously.⁷ The photoemission spectra were obtained with a commercial double-pass cylindrical mirror analyzer with angle-resolving modification (Physical Electronics Model 255- GAR) and a high-intensity discharge lamp. The angular acceptance used was $\pm 6^{\circ}$ and the analyzer band pass was nominally 0.5 eV. Improved energy and angular resolution did not significantly modify the results presented here. The sample consisted initially of a polycrystalline Nb foil $(0.002$ in. thick) which was cleaned in situ by resistive heating to 2200 \degree C for several minutes. Auger spectroscopy, work-function behavior,⁷ and the ultraviolet-photoelectron spectra themselves confirmed that the surface was intially clean. The prolonged heating caused significant grain growth, resulting in large $(\simeq 10 \text{ mm})$ single crystals of Nb(110) as confirmed by low-energy electron diffraction (LEED).

Figure 1 shows the results for three photon energies. The spectra are plotted as a function of