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Magnetic susceptibility of transition-metal alloys with the hcp structure

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An investigation was made of the angular dependences of the magnetic susceptibility of Ru–Nb, Re–W, and Os–Re alloy single crystals in the hcp structure range. The published values of the electron specific heat were used to estimate the spin susceptibility. The principal values of the orbital component of the susceptibility ($\chi_{\parallel \mathrm{orb}}$ and $\chi_{\perp \mathrm{orb}}$) were determined on the assumption of isotropy of the spin contribution to the susceptibility. It was found that alloying had the following effects: the orbital contributions and the anisotropy $\Delta\chi$ of the susceptibility increased in the case of the Ru–Nb alloys; the spin contribution became greater but the orbital susceptibility and the anisotropy $\Delta\chi$ decreased in the case of the Re–W system; the orbital contributions became greater but $\Delta\chi$ was not affected for Os–Re. It was concluded that the addition of the second metal altered the overlap of the wave functions of the *d* electrons.

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Transition metals with the hcp structure can be divided into three groups in accordance with the sign and magnitude of the magnetic susceptibility anisotropy.[1] The first group (Sc, Y) is characterized by negative and moderate values of $\Delta\chi$ ($\Delta\chi = \chi_\parallel - \chi_\perp$). The second group (Ti, Zr, and Hf) has the largest and positive values of $\Delta\chi$. In the case of the third group (Re, Ru, and Os) the difference between the susceptibilites $\Delta\chi$ is negative and minimal. Metals in the first and second groups form practically no alloys with the hcp structure. Only the third group has a limited solid-solution range. Studies of the anisotropy of the magnetic susceptibility of the alloys is of interest because it provides information on the magnetism of weakly magnetic transition metals and its relationship to the electron structure.

We investigated Ru–0.7 wt.% Nb, Re–3 wt.% W, and Os–20 wt.% Re alloys. Single crystals were prepared by zone melting. The magnetic susceptibility was measured by the Faraday method using spherical samples in fields up to 11 kOe between liquid hydrogen and room temperatures. The angular dependences of the magnetic susceptibility were determined and the temperature dependences of χ were found along the principal directions [$\chi_\parallel(T)$ and $\chi_\perp(T)$]. A comparison was made with the magnetic susceptibilities of the corresponding pure metals.

We shall start considering the results by comparing the angular dependences of the susceptibility of the alloys with $\chi(\varphi)$ for the pure metals. In the pure state the magnetic susceptibility is strongest when the magnetic field is perpendicular to the hexagonal axis, i.e., $\Delta\chi = \chi_\parallel - \chi_\perp < 0$. A similar relationship between $\chi_\parallel$ and $\chi_\perp$ is also observed for the alloys: $\chi_\perp > \chi_\parallel$ (Table I).

TABLE I. Electron density (e/a), principal values of magnetic susceptibility ($\chi_\parallel$ and $\chi_\perp$), average magnetic susceptibility of polycrystalline samples [$\chi_{\mathrm{poly}} = (\chi_\parallel + 2\chi_\perp)/3$], susceptibility anisotropy ($\Delta\chi = \chi_\parallel - \chi_\perp$), and temperature coefficients of susceptibility ($d\chi_\parallel/dT$, $d\chi_\perp/dT$) of pure metals and alloys.

Alloy	e/a	$\chi_\parallel$*	$\chi_\perp$*	χ^*_{poly}	$\Delta\chi$*	$d\chi_\parallel/dT$**	$d\chi_\perp/dT$**
Ru	8	35.2±0.2	44.2±0.2	41.2	−9.0	1.4	1.2
0,7% Nb	7.97	35.8	47.7	43.7	−11.9	1.4	1.6
Re	7	68.3	73.0	69.8	−5.4	3.7	2.0
1,0% W	6.99	69.8	74.1	72.7	−4.3	3.3	2.2
3,0% W	6.97	72.8	74.6	74.0	−1.8	3.7	2.2
Os	8	5.4	12.6	10.2	−7.2	0.8	0.3
10% Re	7.9	10.8	19.7	16.7	−8.9	0.7	0.1
20% Re	7.8	22.7	30.7	28.0	−8.0	0.4	0.35

*Values given in units of 10^{-6} cm^3/mole at 293 °K.

**Coefficients $d\chi_{\parallel,\perp}/dT$ found by linear approximation of dependences $\chi_{\parallel,\perp}(T)$ in the range 150–250 °K, given in units of 10^{-8} cm$^3 \cdot$ mole$^{-1} \cdot$ deg^{-1}.

However, the anisotropy $\Delta\chi$ varies in a different way in each alloy system. In the case of the Ru–Nb system (Fig. 1) the anisotropy of χ increases because of an increase in the transverse component of the susceptibility ($\chi_{\parallel}$ is practically unaffected). In the case of the alloys of rhenium with tungsten (Fig. 2) the anisotropy $\Delta\chi$ decreases mainly because of a change in the longitudinal component of the susceptibility ($\chi_{\perp}$ is not greatly affected). In the Os–Re alloys the anisotropy of χ (Fig. 3) is practically unaffected ($\chi_{\parallel}$ and $\chi_{\perp}$ increase uniformly).

On the whole, the addition of a second metal always increases the principal values of the magnetic susceptibility ($\chi_{\parallel}$ and $\chi_{\perp}$) to a greater or smaller degree. Consequently, there is an increase in the value of χ_{poly}, found by the usual averaging in the case of uniaxial crystals: $\chi_{\text{poly}} = (\chi_{\parallel} + 2\chi_{\perp})/3$ (Table I).

We shall now consider the temperature dependences of the magnetic susceptibility. Measurements of $\chi(T)$ show that χ of the alloys increases with rising temperature and the rule established for pure metals is still obeyed: the temperature coefficient is greater for the smaller component of the susceptibility. For our alloys we have $\chi_{\perp} > \chi_{\parallel}$ and $d\chi_{\parallel}/dT > d\chi_{\perp}/dT$ (Table I). Alloying alters slightly the value of $d\chi/dT$ compared with pure metals. In the case of the alloys of rhenium with tungsten and of ruthenium with niobium the temperature dependence of χ is practically the same as for the pure metals, whereas in the Os–Re system the derivative $d\chi_{\parallel}/dT$ decreases compared with $d\chi_{\parallel}/dT$ of pure osmium.

ANALYSIS OF THE RESULTS

The following topics are of the greatest interest: 1) the change in the value of χ_{poly} and in the principal components of χ as a result of alloying; 2) the change in the anisotropy $\Delta\chi$ as a result of alloying. The measured susceptibility of transition metals is known to be a sum of a number of components:

$$\chi_{\text{meas}} = \chi_{\text{dia}} + \chi_{\text{sp}} + \chi_{\text{orb}}, \tag{1}$$

where χ_{dia} is the diamagnetic susceptibility of the ion cores, χ_{sp} is the paramagnetic spin susceptibility of the conduction electrons enhanced by the exchange interaction, and χ_{orb} is the orbital paramagnetic susceptibility of the d electrons.

The diamagnetism of the conduction electrons in transition metals is usually ignored assuming that the magnetic moment is created mainly by the d electrons with a large effective mass. The value of χ_{sp} is estimated, without allowance for the exchange interaction, from the electron specific heat data. If we take the tabulated values of χ_{dia} and if we know χ_{sp} (from γ), we can estimate the orbital component of the susceptibility. The observed anisotropy is usually attributed to the orbital contribution.[5, 6]

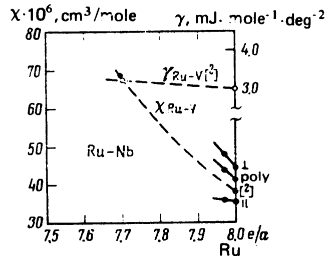

FIG. 1. Dependences of the magnetic susceptibility at right-angles to the c axis (⊥) and parallel to the c axis (||), and of the total susceptibility χ_{poly} on the electron density in Ru–Nb alloys. The dashed curves are the published values of the electron specific heat (γ) and magnetic susceptibility.

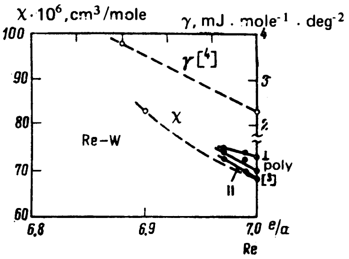

FIG. 2. Dependences of the magnetic susceptibility at right-angles to the c axis (⊥) and parallel to the c axis (||), and of the total susceptibility χ_{poly} on the electron density in Re–W alloys. The dashed curves are the published values of the electron specific heat (γ) and magnetic susceptibility.

We shall now compare the results obtained with the published values of the magnetic susceptibility and electron specific heat of polycrystalline samples of these or similar alloys. In the case of the Ru–Nb system we are not aware of any data on χ or γ in the range of electron densities of interest to us, but there have been investigations of χ and γ of the Ru–V alloys in the hcp structure range. Since niobium is an analog of vanadium (in respect of the electron density and crystallographic structure), we can compare χ_{poly} (calculated from our results by averaging the principal values) with the published data[2] Fig. 1). We can see that the slope of $\chi_{\text{poly}}(e/a)$ of the Ru–Nb alloys is identical with the slope of the dependence $\chi(e/a)$ for the Ru–V alloys. A comparison of our results with those published for the Re–W and Os–Re systems is made in Figs. 2 and 3. In the case of alloys of rhenium with tungsten the value of χ_{poly} depends on e/a in the same way as the results of Booth.[3] However, there is no such agreement in the case of the Os–Re system. The same figures include the electron-density dependences of the electron specific heat of the Ru–V,[2] Re–W,[4] and Os–Re[4] alloys in the range of solid solutions with the hcp structure.

Next, we shall assume that the spin component of the susceptibility, given by Eq. (1), is governed by the

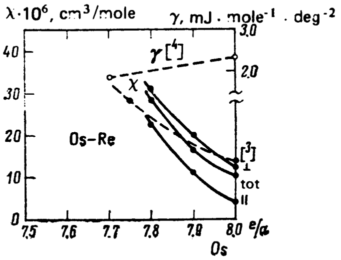

FIG. 3. Dependences of the magnetic susceptibility at right-angles to the c axis (⊥) and parallel to the c axis (||), and of the total susceptibility χ_{poly} on the electron density in Os–Re alloys. The dashed curves are the published values of the electron specific heat (γ) and magnetic susceptibility.

TABLE II. Diamagnetic susceptibility of ion cores (χ_{dia}), electron specific heat (γ), coefficient of electron–phonon enhancement of specific heat (λ) calculated from γ allowing for electron–phonon interaction, spin susceptibility (χ_{sp}), and orbital susceptibilities ($\chi_{\parallel\, orb}, \chi_{\perp\, orb}$) of pure metals and alloys.

Alloy	χ^*_{dia} [8]	γ^{**} [7]	λ [7]	χ^*_{sp}	$\chi^*_{\parallel orb}$	$\chi^*_{\perp orb}$
Ru	18	2.95	0.38	30	23.2	32.2
0.7% Nb	»			30.3	23.5	35.4
Re	12	2.29	0.46	21	59.3	64
1% W	»			23.4	58.4	62.7
3% W	»			28.8	56.0	57.8
Os	11	2.3	0.39	22	−5.6	1.6
10% Re	»			21	+0.8	9.7
20% Re	»			19.8	14.0	22

*These values are given in units of 10^{-6} cm^3/mole at 293 °K.
**Values of γ given in units of mJ · mole^{-1} · deg^{-1}.

density of states at the Fermi limit and is an isotropic quantity. Using the electron-density dependences of γ in the hcp structure range of the investigated systems, we shall determine the spin susceptibility of our alloys allowing for the electron–phonon enhancement of the electron specific heat.[7] The results are presented in Table II. The greatest change in χ_{sp} occurs on addition of tungsten to rhenium. In the case of ruthenium the addition of niobium has practically no effect on χ_{sp} and the addition of rhenium to osmium reduces somewhat χ_{sp}. Such changes in the spin component deduced from the experimental data on γ are in agreement with the theoretically calculated density-of-states curves.[9, 10] It follows from them that the Fermi limit of rhenium[9] lies on a steep slope of the $N(E)$ curve and a reduction in the electron density should result in a strong rise of $N(E)$. In the case of osmium and ruthenium[10] the Fermi limits are in the regions of flat minima. Consequently, there are only slight changes in the density of states because of a change in the electron density.

We shall assume that the susceptibility anisotropy is governed by its orbital component, i.e.,

$$\chi_{\parallel}=\chi_{dia}+\chi_{sp}+\chi_{\parallel orb},$$
$$\chi_{\perp}=\chi_{dia}+\chi_{sp}+\chi_{\perp orb},$$

and we shall then determine the principle values of the orbital components of the susceptibility of the alloys (Table II). It is clear from Table II that the main change in the susceptibility on addition of niobium to ruthenium occurs because of an increase in the orbital component of the susceptibility at right-angles to the hexagonal axis. Consequently, the susceptibility anisotropy increases.

When tungsten is added to rhenium, the increase in the spin susceptibility plays an important role and the orbital susceptibility decreases along both principal directions but the reduction is greater, as in the case of the Ru–Nb system, at right-angles to the hexagonal axis. Consequently, the anisotropy decreases.

In the case of the Os–Re system a similar analysis becomes complicated by the fact that the longitudinal component of the susceptibility of pure osmium is diamagnetic. It is possible that this is the result of the approximate nature of our estimates: we have ignored the exchange interaction of the conduction electrons which enhances the spin paramagnetism and we have neglected the conduction-electron diamagnetism. This diamagnetism may be important in osmium. However, within the framework of the estimates made above, the addition of rhenium makes the orbital contribution paramagnetic along both principal directions and this contribution increases with the rhenium concentration. The susceptibility anisotropy is practically unaffected.

TABLE III. Atomic radii and lattice parameters.[11]

Element	R_A, Å	a, Å	c, Å
Ru	2.72	2.700	4.28
Nb	2.92		
Re	2.76	2.755	4.449
W	1.4		
Os	2.70	2.730	4.310

Consequently, we may conclude that there is a considerable change in the orbital component in the susceptibility as a result of alloying and the anisotropy may increase (Ru–Nb) or decrease (Re–W). According to the theory of Ducastelle and Cyrot-Lackmann,[5] the anisotropy of the orbital paramagnetism is associated with the relative change of the overlap integrals due to a change in the atomic distances. Introduction of a second metal into the investigated alloys not only reduces the electron density but also alters somewhat the atomic distances. A reduction in the electron density alters the spin component of the susceptibility and the isotropic part of the orbital component. Since the dimensions of the second-metal atoms differ from those of the matrix atoms (Table III), the addition of the second metal alters the atomic distances and, consequently, the overlap of the wave functions of the d electrons. In the case of the Os–Re alloys the atomic radii of osmium and rhenium are similar and the anisotropy of the orbital susceptibility is practically unaffected.

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