

PARAMAGNETIC SUSCEPTIBILITY OF YTTRIUM AND RHENIUM SINGLE CRYSTALS

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Submitted July 26, 1968

Zh. Eksp. Teor. Fiz. 56, 139–143 (January, 1969)

The temperature dependence of the paramagnetic susceptibility of yttrium and rhenium single crystals is investigated for two directions of the field relative to the hexagonal axis, $c \parallel H$ and $c \perp H$, at temperatures from 20.4 to 293° K. It is found that $\chi_{\perp} > \chi_{\parallel}$ in both metals. The orbital contribution to the susceptibility is estimated by comparing χ_{meas} with χ calculated on basis of the band theory. In the metals investigated, the temperature-dependence coefficient $d\chi/dT$ is positive. Possible causes of the observed temperature dependence are discussed.

1. To study further the anisotropy of the paramagnetic susceptibility of metals with hexagonal close-packed structure^[1], we investigated the susceptibility of single crystals of rhenium and yttrium.

Bommer^[2] first observed a weak increase of the susceptibility of metallic yttrium when the temperature was decreased from room temperature to 90° K. Later Chechernikov^[3], in measurements on single-crystal and polycrystalline samples of yttrium, established that the Curie-Weiss law holds in a wide temperature range (from 80 to 1000° K). The susceptibility of rhenium was measured^[4] only on polycrystalline samples at high temperatures; a positive sign of the coefficient $d\chi/dT$ was established.

We investigated in the present work crystals grown by zone melting¹⁾. The purity of the different rhenium crystals was sufficiently high (~99.98%), and the results of the susceptibility measurements were uniform for all of them. The yttrium was less pure (99.8%) and exhibited an appreciable dependence of the susceptibility (in magnitude and in temperature radiation) on the content of the ferromagnetic impurities in the metal. We discuss here the characteristic results for the purest rhenium crystals ($\rho_{293^{\circ}K}/\rho_{4.2^{\circ}K} = 1020$) and yttrium Y1 ($\rho_{293^{\circ}K}/\rho_{4.2^{\circ}K} = 14$), and also present for comparison results obtained for the sample Y2 ($\rho_{293^{\circ}K}/\rho_{4.2^{\circ}K} = 11$), which contains a larger percentage of ferromagnetic impurities than Y1 (see the table). The samples were prepared in the form of spheres of ~1.5 mm diameter. The hexagonal axis was revealed by etching the yttrium samples with nitral and the rhenium samples with concentrated nitric acid. The measurements were

made by the same method as in^[1]. The relative measurement error was ~1%. The sample was mounted in such a way that the suspension axis was perpendicular to the direction of the hexagonal axis in the sample. This made it possible to obtain different crystallographic orientations in a plane containing the hexagonal axis, by rotating the magnet around the sample.

The dependence of the susceptibility of yttrium and rhenium on the direction of the magnetic field was determined in a field $H = 10.2$ kOe (Fig. 1). Symmetrical curves were obtained with a period of 180°. For both metals, the susceptibility in a direction perpendicular to the hexagonal axis (χ_{\perp}) is larger than in the direction parallel to this axis (χ_{\parallel}). In a plane perpendicular to the hexagonal axis, the susceptibility is isotropic within the limits of experimental error. The anisotropy of the susceptibility in yttrium and rhenium is much smaller than in zirconium ($\chi_{\parallel} = 147$ and $\chi_{\perp} = 86 \times 10^{-6}$ e.m. units/mole^[1]).

Measurements of the susceptibility for two directions of the field relative to the hexagonal axis ($H \perp c$ and $H \parallel c$) at room temperature and at liquid-hydrogen temperature have shown that the susceptibility in fields from 5 to 15 kOe does not depend on H. In Table I are shown values of χ_{\parallel} and χ_{\perp} at room temperature, and also the values of the susceptibility for polycrystals, calculated by means of the usual averaging formula

$$\chi_{polycr} = (\chi_{\parallel} + 2\chi_{\perp}) / 3. \tag{1}$$

We present here also the results of measurements of the molar susceptibility, obtained for polycrystalline samples in^[2-6]. Notice should be taken of the good agreement between the values of χ_{polycr} calculated by formula (1) and data by others, with the exception of the

Table I

Sample	% of ferromagnetic impurities	$\chi_{\parallel} \cdot 10^4$	$\chi_{\perp} \cdot 10^4$	$\chi_{polycr} \cdot 10^4$	Data by others
Y1	0.003	174	200	191	191 [2] 370 [3]
Y2	0.035	208	229	222	187 [5] 196 [6]
Re	0.00036	68.3	73	71	65 [4]

1)We are grateful to N. A. Koroleva for supplying the rhenium crystals and G. E. Chuprikov for the yttrium crystals.

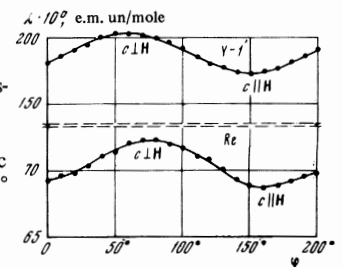


FIG. 1. Dependence of the susceptibility of single crystals of yttrium and rhenium on the angle between the direction of the magnetic field and the hexagonal axis at 293° K.

results of^[3]. This is apparently due to the fact that the yttrium investigated in^[3] contained a large amount of rare-earth metal impurities (0.3%).

The temperature dependence of the susceptibility were measured from 20.4 to 293°K in a constant field $H = 10.2$ kOe for the two aforementioned directions of the field relative to the hexagonal axis. As seen from Figs. 2 and 3, the $\chi(T)$ curves of yttrium Y1 and of rhenium are similar: the coefficient of the temperature dependence of the susceptibility is positive ($d\chi/dT > 0$) at high temperatures and the susceptibility increases at lower temperatures (in rhenium below 50°K and in yttrium below 110–120°K). For rhenium, in a direction parallel to the hexagonal axis, the temperature dependence of the susceptibility is stronger than in a direction perpendicular to it. In Y1, at temperatures above 120°K, the $\chi(T)$ curves are practically parallel for both field directions relative to the hexagonal axis. In Y2, in the entire measured temperature interval, an appreciable growth of the susceptibility is observed with decreasing temperature.

2. The investigated metals, yttrium and rhenium are Pauli paramagnets, as is evidenced by the absence of a Curie-Weiss dependence of the susceptibility on the temperature (an exception is sample Y2, for which the situation will be discussed later). In the band theory, the Pauli susceptibility is determined by the density of states on the Fermi boundary $N(E_F)$:

$$\chi_{sp} = \mu_B^2 N(E_F),$$

where μ_B is the Bohr magneton, and $N(E_F)$ is calculated from the coefficient of the electronic specific heat γ : $N(E_F) = 3\gamma/\pi^2 k^2$. On the basis of the experimental data on the electronic specific heat, we determine the values of the spin susceptibility of yttrium and rhenium. From a comparison of χ_{polycr} with χ_{sp} (see Tables I and II) we see that the measured susceptibility is higher than that calculated from the band theory, as was noted

Table II

Metal	γ , mJ/mole-deg ²	$\chi_{sp} \cdot 10^4$	$\chi_{orb} \cdot 10^6$	Δ , eV	E_F , eV
Y	10,2 [7]	132	~ 60	~ 2	6,3 ^[13]
Re	2,45 [8]	29,7	~ 40	~ 7,5	11,2 ^[14]

for other transition metals^[6]. The difference between the measured and spin susceptibilities is attributed to the presence of a non-zero orbital magnetic moment in metals with partly-filled d- or p-bands^[9,10]. In this connection, the gyromagnetic ratio should differ from $g = 2$ by an appreciable amount. As shown by measurements^[11], $g = 1.2$ in vanadium. This indicates that the contribution of the orbital magnetic moment to the susceptibility is comparable with the spin contribution. Assuming that the exchange and correlation effects cancel each other, the paramagnetic susceptibility of a transition metal in the absence of localized magnetic moments is represented^[10] as the sum of the following contributions:

$$\chi = \chi_{sp} + \chi_{orb} + \chi_{dia},$$

where χ_{sp} is the spin susceptibility of the s- and d-electrons, χ_{orb} is the orbital susceptibility, and χ_{dia}

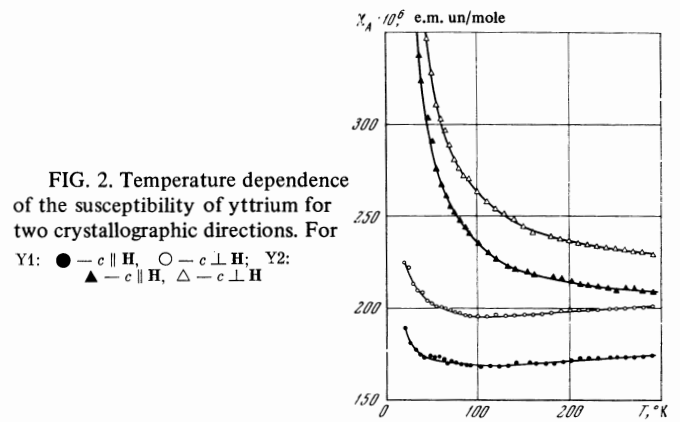


FIG. 2. Temperature dependence of the susceptibility of yttrium for two crystallographic directions. For Y1: ● — $c \parallel H$, ○ — $c \perp H$; Y2: ▲ — $c \parallel H$, △ — $c \perp H$

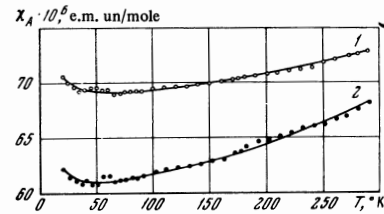


FIG. 3. Temperature dependence of the susceptibility of rhenium in two crystallographic directions. Curve 1 — $c \perp H$, 2 — $c \parallel H$.

is the diamagnetic susceptibility of the ionic core and of the free electrons.

Estimates of χ_{orb} without allowance for the diamagnetic contribution are given in Table II. According to Orgel^[12], the orbital contribution to the susceptibility is determined by the expression

$$\chi_{orb} = 2\mu_B^2 n(10 - n) / 5\Delta,$$

where n is the number of electrons per atom and Δ is an energy parameter of the order of the width of the d-band. Hence, knowing χ_{orb} , we can calculate Δ (see Table II). In the calculation of the electronic structure of yttrium^[13] and^[14] by the method of joined plane waves, the values obtained for the Fermi energy E_F were 6.3 eV for yttrium and 11.2 eV for rhenium. Thus, the calculated values of E_F and the values of Δ obtained from experiment are of the same order of magnitude, thus indicating that the foregoing estimates are reasonable.

The experimentally observed anisotropy of the susceptibility is most probably due to the anisotropy of the orbital contribution, although the possibility of anisotropy of the diamagnetic component of the susceptibility is not excluded.

As was already indicated above, the temperature dependence of the susceptibility of Re and Y1 are described by curves with minima. The increase of the susceptibility at low temperatures is connected with the presence of a small amount of ferromagnetic impurities in the samples. In Y2, which contains an appreciable number of these impurities (particularly gadolinium—0.02%), there appears a contribution to the susceptibility from the magnetic moments localized on the impurities, with a clearly pronounced Curie-Weiss temperature dependence. The latter masks the weak true tempera-

ture dependence of the susceptibility of yttrium.

According to the classification of Kriessman^[15], the temperature dependence of the susceptibility of transition metals is determined by the position of the Fermi boundary on the plot of the density of states. In metals with an odd number of d-electrons, E_F lies at the maximum of the state-density curve and $d\chi/dT < 0$, while in metals with an even number of d-electrons it lies in the minimum and $d\chi/dT > 0$. In both yttrium and rhenium, the Fermi boundary should lie at the maximum of the state-density curve. This is evidenced by the large value, compared with the nearest neighbors, of the molar susceptibility in these metals: $\chi_{Zr} = 119$ ^[11], $\chi_W = 55$ ^[41], and $\chi_{Os} = 9 \times 10^{-6}$ e.m. un/mole^[41]. Indeed, as seen from the state-density curve plotted from the data on the electronic specific heat for the metals of the 4d- and 5d- group^[16], the Fermi boundary in rhenium is located at the minimum. Accordingly, the coefficient $d\chi/dT$ in rhenium should be positive, as is indeed observed experimentally. The position of E_F of yttrium on the density of states curve is shown arbitrarily. Judging from the form of the experimentally observed temperature dependence of the susceptibility for pure yttrium (if we assume that the decisive role in the temperature dependence of the susceptibility is played by the spin contribution), the Fermi boundary in yttrium is not at the maximum of the state-density curve, or else the maximum in this region of the electron concentrations has a complicated form.

Another reason for the appearance of a temperature dependence of the susceptibility may be the presence of small groups of carriers. The Fermi surfaces of yttrium^[13] and rhenium^[14], constructed on the basis of the band-structure calculations, are complicated in form. Measurements of the de Haas-van Alphen effect in rhenium^[17] have confirmed, in main outline, the theoretical model. Thus, the presence of small groups of carriers, with an anisotropic equal-energy surface, is quite probable for the proposed Fermi surfaces. These carrier groups, possibly, make different contributions to the susceptibility, depending on the direction of the magnetic field relative to the crystal. Moreover,

starting with a certain temperature corresponding to the energy parameters of this small group, the magnitude and anisotropy of this contribution should change. Such a picture is observed in rhenium and zirconium^[11]. This effect may not appear in yttrium, owing to the slight purity of the investigated crystals.

¹N. V. Volkenshtein, É. V. Galoshina, and N. I. Shchegolikhina, *Fiz. Metal. Metallov.* **25**, 180 (1968).

²H. Bommer, *Z. Electrochem.* **45**, 357 (1939).

³V. I. Chechernikov, Iuliu Pop, V. F. Terekhova, and V. E. Kolesnichenko, *Zh. Eksp. Teor. Fiz.* **46**, 444 (1964) [*Sov. Phys.-JETP* **19**, 298 (1964)].

⁴H. Kojime, R. S. Tebble, and D. E. G. Williams, *Proc. Roy. Soc.* **A260**, 237 (1961).

⁵O. M. Hilal, *J. Chem. Soc.*, 135 (1949).

⁶N. V. Volkenshtein and É. V. Galoshina, *Fiz. Metal. Metallov.*, **20**, 368 (1965).

⁷H. Montgomery and G. P. Pells, *Proc. Phys. Soc.* **78**, 622 (1961).

⁸E. C. Morin, J. P. Maita, *Phys. Rev.* **129**, 1115 (1963).

⁹R. Kubo and Y. Obata, *J. Phys. Soc. Japan* **11**, 547 (1956).

¹⁰A. M. Clogston, V. Jaccarino and Y. Yaffet, *Phys. Rev.* **134**, A650 (1964).

¹¹R. Huguenin and D. Baldock, *Phys. Rev. Lett.* **16**, 795 (1966).

¹²L. E. Orgel, *J. Phys. Chem. Sol.* **21**, 123 (1956).

¹³T. L. Loucks, *Phys. Rev.* **144**, 504 (1966).

¹⁴L. F. Mattheis, *Phys. Rev.* **151**, 450 (1966).

¹⁵C. J. Kriessman and H. B. Callen, *Phys. Rev.* **94**, 837 (1954).

¹⁶A. Katsuki and M. Shimizu, *J. Phys. Soc. Japan* **21**, 279 (1966).

¹⁷A. C. Thorsen, A. S. Joseph and L. E. Valby, *Phys. Rev.* **150**, 523 (1966).

Translated by J. G. Adashko