Superconductivity and crystal structure of high-pressure phases in the Ta–Ru–H system

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The solubility of hydrogen in tantalum–ruthenium alloys containing 22.6 and 31 at. % ruthenium, at 300°C and hydrogen pressures up to 80 kbar, was studied; the crystal structure of the hydrogenous phases was examined with x rays; the temperatures T_c of the transition to the superconducting state were determined. Each of the alloys exhibited phases with a hydrogen/metal atomic ratio $n \sim 1$; with an orthorhombically distorted hcp metal lattice and $T_c \sim 3$ K, whereas the original alloys do not become superconducting above 2 K.

When hydrogen dissolves in the majority of superconducting metals (in particular vanadium, niobium, tantalum, tectnetium, and rhenium) and alloys, the superconductivity is suppressed.[1,2] Only a few definite exceptions have been found, namely (1) the occurrence of superconductivity in hydrides of palladium and palladium-based alloys[1,3], (2) the considerable rise in the temperature T_c of the transition to the superconducting state when hydrogen saturates thorium[4] and various alloys of niobium with rhenium,[5] rhodium,[6] palladium,[6,7] and palladium plus molybdenum or tungsten.[7] Further investigations have shown that the hydrides of palladium and probably of thorium differ qualitatively from the superconductors studied previously: there is a considerable contribution to the electron–phonon interaction these hydrides from the interaction of the electron–phonon interaction in these hydrides from the interaction of the electrons with the optical lattice vibrations.[1,8] If we note moreover that, because of the very small mass and simple electron structure of the atoms of one component (hydrogen), the metal hydrides are suitable models for testing and refining the existing theories of superconductivity in alloys, it becomes quite clear why there has been such interest in the superconducting properties of metal–hydrogen systems, ever since the discovery of superconducting hydrides.

The present state of our knowledge, however, does not yet allow an a priori prediction of how dissolved hydrogen should influence T_c in any particular meals and alloys. Moreover, for alloys there is usually not even the basic information, needed to calculate T_c, concerning the crystal structure of possible hydrogenous phases. An interesting problem at the present time is therefore the acquisition of experimental results by studying metal–hydrogen systems that are of possible significance as regards superconductivity, with the widest possible range of hydrogen concentrations, and in particular the search for metals and alloys in which dissolved hydrogen causes a considerable increase in T_c.

The present paper concerns the preparation and study of solid solutions of hydrogen in tantalum–ruthenium alloys, which are closely similar to niobium-ruthenium ones; in the periodic table, tantalum falls immediately below niobium. An increase in T_c upon hydrogenation has been found[5] for niobium with 20, 25, and 33 at.% ruthenium. We examined Ta–Ru–H solutions formed at high pressure in an atmosphere of excess molecular hydrogen and based on tantalum with 22.6 and 31 at.% ruthenium.

1. SAMPLE PREPARATION AND EXPERIMENTAL METHOD

To prepare the alloys, weighed amounts of powders (~ 40 mesh) of tantalum (99.99%) and ruthenium (99.998%) were mixed, pelletized under 20 kbar at room temperature, and then remelted in an electric arc furnace in argon at ~ 200 torr. The ingots were annealed at 1800°C in a vacuum of $\sim 10^{-6}$ torr for 24 h and then cooled in the furance. The ruthenium content in the original powder mixes was 25 and 33 at.%. Chemical analysis of the ingots with a CAMEBAX-MBX microanalyzer and a Link 860-500 energy-dispersion x-ray spectrometer showed that the alloys lost ruthenium during melting, reaching 22.6 and 31.0 ± 0.4 at.%. Samples were cut from ingots by spark machining the damaged surface layer ~ 0.05 mm was ground off, and then a layer ~ 0.03 mm was removed by electropolishing in sulfuric acid. The final size of the samples was $\sim 3 \times 0.35$ mm.

The samples were saturated with hydrogen by keeping them in an atmosphere of molecular hydrogen at 300°C and pressures up to 80 kbar for 24 h, by a technique described previously.[2] Preliminary experiments had shown that the hydrogen content of these samples remains almost unchanged for holding times longer than 10 h. The error in determining the pressure did not exceed ±5%; the temperature was kept constant to within ± 7°C while holding the samples under hydrogen at high pressures. After the end of the process, the pressure chamber and the samples were cooled to ≈ -180°C, the pressure was lowered to atmospheric, the samples were extracted, and to prevent hydrogen loss they were kept in liquid nitrogen until the start of the measurements.

The stability of the Ta–Ru–H samples as regards distingeration into the metal and molecular hydrogen at atmospheric pressure decreased with increasing hydrogen content in the alloys, and a noticeable release of hydrogen from samples with hydrogen/metal atomic ratio $n \sim 1$ occurred for -90 to -60°C; at room temperature, most of the hydrogen was evolved in a few seconds. Nevertheless, it was not less, it was not entirely released from samples at room temperature within any reasonable time (a few days): the residual content was $n \sim 0.05$ for $Ta_{77.4}Ru_{22.6}$ – H and $n \sim 0.01$ $Ta_{69}Ru_{31}$ – H. Accordingly, the total hydrogen content in the samples was determined in two stages. First, they were placed in a graduated glass con-
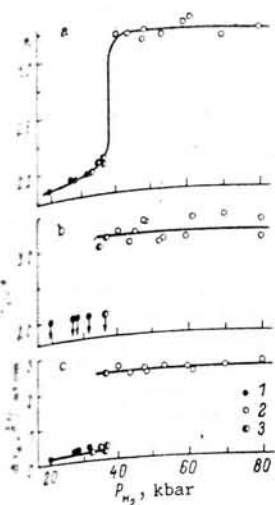
tainer at room temperature, previously filled with silicone, and the amount of hydrogen evolved was estimated from the volume of silicone displaced. They were next placed in a container with a known volume, previously evacuated, and residual hydrogen was removed from them by heating to 500°C for 10 min, the amount of this hydrogen being estimated from its pressure. The relative accuracy of determination of the total hydrogen content of the samples was about ± 5%.

The initial tantalum–ruthenium alloys and the solutions of hydrogen in them were polycrystalline. The samples were studied by x-ray diffraction at −190°C using the photographic technique, a DRON-2.0 diffractometer, and Cu Kα radiation. They were in contact with the air for about 1 sec during transfer from the nitrogen dewar to the cryostat of the x-ray equipment.

The T_c values were found by induction for $T \geq 2$ K; the sample temperature did not rise above the boiling point of nitrogen during transfer to the cryostat.

In the study of Ta–Ru–H solutions, each of the samples synthesized was divided into two parts, one used for the x-ray investigation and the other to determine T_c. The final concentration of hydrogen in the two parts was the same, within the error of measurement, after completion of all operations.

EXPERIMENTAL RESULTS AND DISCUSSION

The x-ray measurements showed that at −190°C and atmospheric pressure the initial alloy samples containing 22.6 and 31 at.% ruthenium had respectively a disordered bcc (α) structure (a = 3.316 ± 0.002 Å; the volume V_a per metal atom is $a^3/2 = 18.63 \pm 0.03$ Å^3/atom) and an ordered (αor) structure of the cesium chloride type (a = 3.194 ± 0.002 Å; $V_a = a^3/2 = 16.29 \pm 0.03$ Å^3/atom); these results are in agreement with published values.[9]
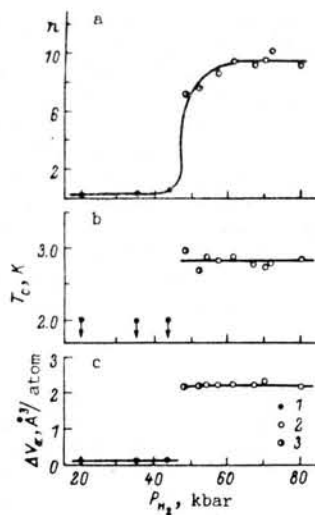

FIG. 2. Results for $Ta_{69}Ru_{31}$—H solid solutions: 1) α or; the rest of the notation as in Fig. 1.

No previous study has been made of the superconducting properties of tantalum–ruthenium alloys. However, on the basis of Matthias'[10,11] general conclusions regarding these properties for transition metal alloys, we can expect that T_c for our alloys will be noticeably less than the value (∼ 0.25 K) for the niobium–ruthenium alloys[5] with the same range of ruthenium concentrations. An estimate by Miedema's method[12] with the parameters given there leads to $T_c \leq 0.18$ K and $T_c \leq 0.03$ K for $Ta_{77.4}Ru_{22.6}$ and $Ta_{69}Ru_{31}$ respectively. Our measurements showed that neither alloy is superconducting at $T \geq 2$ K.

Figures 1 and 2 show the main results of the present study for Ta–Ru–H solutions.

It is seen from Figs. 1a and 1c that, at 300°C, raising the hydrogen pressure to ∼ 32 kbar causes a monotonic increase in the equilibrium hydrogen concentration in the α alloy $Ta_{77.4}Ru_{22.6}$ to n ∼ 0.13, accompanied by an increase in the bcc lattice parameter of the alloy. At higher pressures, the $Ta_{77.4}Ru_{22.6}$—H system forms a new phase (ε' solution) in which the hydrogen concentrations (n = 1.10 ± 0.06) and the volumes V_a per metal atom are constant within the experimental error when the synthesis pressure varies up to P_{H_2} = 80 kbar. X-ray examination showed that at atmospheric pressure and −190°C this phase has an orthorhombically distorted hcp metal lattice; the mean lattice parameters are a_r = 5.188 Å, b_r = 4.951 Å, c_c = 2.966 Å, $V_a = a_r b_r c_r/4 = 19.05$ Å^3/atom. To illustrate the nature of the observed distortion, Fig. 3 shows schematically the (00.1) plane of the trebeled unit cell in the hexagonal lattice; the continuous lines mark the orthorhombic cell. In the standard description of the hexagonal structure, with orthorhombic axes Z_r along the hexagonal axis X_h, and Y_r along Z_r, the parameter $a_r \equiv a_h\sqrt{3}$. In ε' solutions $Ta_{77.4}Ru_{22.6}$—H a_r = 5.188 Å ≈ $1.010 c_r\sqrt{3}$; this may be regarded as the result of a uniform compression of the hexagonal lattice in the [10.0] direction.

Further measurements showed that, whereas the original α alloy $Ta_{77.4}Ru_{22.6}$ and the corresponding α hydrogen solutions with n ≤ 0.13 do not become superconducting above 2 K, the ε' solutions do (Fig. 1b). The temperature range of the transition for samples consisting entirely of the ε' phase did not exceed 0.3 K; this increased to ≈ 0.6 K for
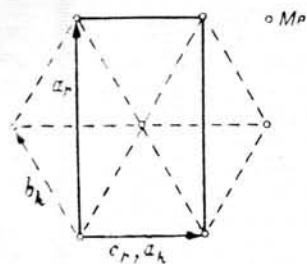
FIG. 3. Schematic of the (00.1) plane of the hexagonal lattice trebled unit cell.

those formed in the $\alpha \to \varepsilon'$ transition region at high pressure and consisting of mixed α and ε' phases. Figure 1b shows the positions of the middle of the superconducting transition range. It is seen that the values of T_c for the ε' solutions $Ta_{77.4}Ru_{22.6}-H$ are, within the experimental variation, independent of the pressure at which the solutions were obtained; the mean $T_c = 3.1$ K.

The properties of the $Ta_{69}Ru_{31}-H$ system showed essentially only a quantitative difference from $Ta_{77.4}Ru_{22.6}-H$. Figure 2 indicates that, at 300°C and pressures up to ≈ 44 kbar, the former system has solutions not superconducting above 2 K, derived from the original α^{or} lattice of $Ta_{69}Ru_{31}$, the concentration reaching $n \approx 0.05$ at $P_{H_2} = 44$ kbar. At higher pressures, an ε' phase is formed, with an orthorhombically distorted hcp metal lattice; the prooperties of this phase are, within the experimental error, independent of the synthesis pressure up to $P_{H_2} = 80$ kbar. The mean metal lattice parameters at atmospheric pressure and at $-190°C$ are $a_r = 5.163$ Å $\approx 1.015 c_r \sqrt{3}$; $b_r = 4.881$ Å; $c_r = 2.937$ Å; $V_a = 18.50$ Å^3/atom; hydrogen concentration $n = 0.95 \pm 0.05$; mean $T_c = 2.8$ K. Thus, in the $Ta_{69}Ru_{31}-H$ system, the ε' phase formation pressure and the amount of orthorhombic distortion of its metal sublattice, represented by the ratio a_r/c_r, increase; the hydrogen concentration and T_c are somewhat less than the corresponding values for the ε' phase in the $Ta_{77.4}Ru_{22.4}-H$ system.

Another point should be noted as regards the structural investigation of Ta–Ru–H solutions. In both the systems examined, the diffraction patterns of samples containing the ε' phase usually showed not only the clear narrow lines of that phase but also two, three, or sometimes four very broad additional lines, which can be assigned to (10.0), (00.2), (10.1), and (11.0) in hexagonal axes. With this interpretation of the lines, the parameters of the corresponding phases with the hcp (ε') metal lattice were $a \approx 2.88$ Å, $c \approx 4.73$ Å, $c/a \approx 1.64$, $V_a \approx (\sqrt{3}/4) a^2 c \approx 17.0$ Å^3/atom for 22.4 at.% ruthenium; $a \approx 2.84$ Å, $c \approx 4.67$ Å, $c/a = 1.64$, $V_a \approx 16.3$ Å^3/atom for 31 at.%. Within the experimental error $\approx \pm 0.02$ A, which is determined mainly by the large width of the diffraction lines, the a and c values for the ε phases in each in each Ta–Ru–H system were the same for all the samples studied.

If we ignore the possible separation of Ta–Ru–H solid solutions into phases with a different ratio of tantalum and ruthenium concentrations (among the many metal–hydrogen systems based on transition metal alloys so far studied, this has been observed[2] in only two systems, Pd–Ni–H and Pd–Pt–H), the values of V_a found for the ε phases can be used to estimate their hydrogen content.

The dependences $\Delta V_a(n)$ of the increase in the volume V_a per metal atom when hydrogen dissolves in transition metals and their alloys are similar and almost linear over wide ranges of hydrogen

concentrations.[2,13] In particular, for tantalum–hydrogen solutions the $\Delta V_a(n)$ observed by various authors have slopes $\beta = (\partial/\partial n)\Delta V_a(n)$ ranging from ≈ 2.3 Å^3/H atom (Fig. 4, continuous line) to ≈ 2.8 Å^3/H atom (Fig. 4, dashed line).[13] It is seen from Fig. 4 that our results for Ta–Ru–H α and α^{or} solutions can be approximated by a straight line with $\Delta V_a/n = (19.05 - 16.63)/1.10 = 2.2 \pm 0.1$ Å^3/atom. This value of β agrees satisfactorily with $\Delta V_a/n = (19.05 - 16.63)/1.10 = 2.2 \pm 0.1$ Å/H atom and $\Delta V_a/n = (18.50 - 16.29)/0.95 = 2.3 \pm 0.15$ Å^3 H atom for the respective ε' solutions $Ta_{77.4}Ru_{22.6}-H$ and $Ta_{69}Ru_{31}-H$.

With $\beta = 2.3$ Å^3/H atom for the ε phases found in the $Ta_{77.4}Ru_{22.6}$ and $Ta_{69}Ru_{31}-H$ systems, we get respectively $n_{cal} = (17.0 - 16.63)/2.3 = 0.16 \pm 0.1$ and $n_{cal} = (16.3 - 16.29)/2.3 = 0 \pm 0.01$. From the low values of n_{cal}, it is logical to suppose that the ε phases are intermediate ones in the separation of Ta–Ru–H ε' solid solutions with $n \sim 1$ into metal and molecular hydrogen. It is most likely that a partial loss of hydrogen from the surface layer of Ta–Ru–H ε samples occurred when these were being transferred to the x-ray cryostat and their surfaces were for about a second in contact with the air; the typical depth of the Ta–Ru and Ta–RU–H sample layer involved in forming the diffraction pattern was only of the order of $1/2\mu \approx 2 \cdot 10^{-3}$ mm, where μ is the linear attenuation coefficient.[14]

One further comment regarding the structural features of these systems. After the hydrogen-saturated $Ta_{77.4}Ru_{22.6}$ samples were heated to 500°C in vacuum, their structure reverted to the original bcc with the original lattice parameter value (and this was evidence that the heating caused fairly complete removal of hydrogen). Similar heating of samples based on $Ta_{69}Ru_{31}$, whose saturation with hydrogen at high pressure was accompanied by formation of the ε' phase, likewise gave a disordered bcc structure (there were no superlattice reflections corresponding to cesium chloride type ordering), and the bcc lattice parameter was the same, within the error of measurement, as the value for the original ordered structure. A check showed that the superlattice reflections also disappear, and the cubic lattice parameter is maintained, in the original $Ta_{69}Ru_{31}$ samples when their surfaces are subjected to mechanical grinding. The disordering of the alloy under plastic deformation during grinding makes it entirely likely that there is no restoration of the structure to the original ordered α^{or} for $Ta_{69}Ru_{31}$ based samples after dehydrogenation, simply because at room temperature (and perhaps for $T \leq 500°C$) that is not the thermodynamic equilibrium structure of the alloy concerned.
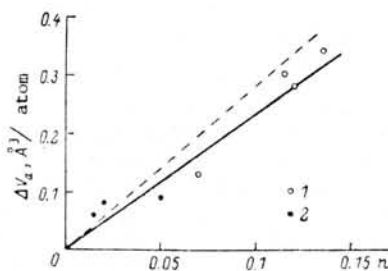

FIG. 4. Volume increase $\Delta V_a(n)$ per metal atom, as a function of the hydrogen concentration n: 1) $Ta_{77.4}Ru_{22.6}-H$; α solutions; 2) $Ta_{69}Ru_{31}-H$ α^{or} solutions (T = -190°C); lines, see text.

Antonov et al.

The results presented above show that in the $Ru_{22.6}$—H and $Ta_{69}Ru_{31}$—H systems phases $Ta_{?.?}$ with n = 1 are formed, based on the orthorhombically distorted hcp metal lattice, with a value of $T_C \approx 3$ K that considerably exceeds those for the original hydrogen-free tantalum—ruthenium alloys. A direct comparison of our results for the structure and hydrogen content of superconducting Ta-Ru-H solutions with published results [5-7] for hydrogenous phases in analogous systems based on niobium is, unfortunately, not possible, because those are multiphase samples. The increase of T_C to $\approx$ 2.5-5 K in Nb–Ru–H, Nb–Pd–H, Nb–Pd–Mo–H, and Nb–Pd–W–H was attributed [5,7] to phases having the fcc metal lattice, but according to other results [6] phases having the bcc metalk lattice have similar T_C values in the Nb–Pd–H and Nb–Rh–H systems.

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Density of states of a zero-gap extrinsic semiconductor in a magnetic field

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The energy dependence of the density of states $\rho_H(E)$ corresponding to $E \to 0$ is studied for a zero-gap type I extrinsic semiconductor in the quantum limit. It is shown that the problem of calculating $\rho_H(E)$ can be reduced to a one-dimensional stochastic problem which can be solved exactly. When short-range impurity interactions are taken into account, a finite density of states is obtained for $E \to 0$. For a scattering potential describing modulation of the gap, the dependence $\rho_H(E)$ exhibits a Dyson singularity.

1. It is a special feature of the type I zero-gap states[1] that there is no gap in the quantum limit in a quantizing magnetic field[2] and in the absence of electron–phonon and electron–impurity scattering. The Green's function of a "Dirac" electron does not depend on the corresponding quantum number (the multiplicity of the degeneracy with respect to this number is $1/2\pi\ell^2 H$) and the density of quantum states has the following "one-dimensional" form:

$$\rho_{0H} = \frac{1}{2\pi \ell_H^2} \frac{1}{\pi\hbar s},\tag{1}$$

where $\ell^2 H = \hbar c/eH$; s is the limiting excitation rate of the spectrum in the Cohen–Blount model.[3] When correlations in the impurity distribution are neglected, Eq. (1) in the linear approximation in the impurity concentrations governs the field dependences of the transport coefficients in the quantum limit (see Ref. 2). It is important for the Shubnikov–de Haas oscillations in the quasiclassical region that Eq. (1) is independent of the energy (see Ref. 4).

We shall study the the behavior of the density of states in the quantum limit for $E \to 0$ taking into account short-range impurity interactions. It is our intention to prove that it is possible to carry out integration with respect to the coordinates transverse to H in the electron–impurity Hamiltonian provided the

field is extremely strong and the matrix elements of the transition to nonzero Landau subbands can thus be neglected; this effectively reduces the calculation of $\rho_H(E)$ to the well-known one-dimensional problem (d = 1).[5-7]

2. We shall consider the motion of conduction electrons which in a type I zero-gap state in quantizing magnetic fields can be described by the Dirac Hamiltonian[8]

$$\mathcal{H}_0 = s\alpha\left(p - \frac{e}{c}A\right)\tag{2}$$

and assume short-range interactions with impurities described by a potential V(x). In Eq. (2), α are Dirac matrices and it is convenient to choose the vector potential in the axial gauge

$$A = \frac{1}{2}[H \times r], \quad H \parallel z.\tag{3}$$

In the absence of interaction, the normalized ℓ-fold degenerate ($\ell = L^2/2\pi\ell^2 H$) stationary type I zero-gap states with an energy $E_{n=0,\,e_z=1,\,k_z} = \pm\hbar s k_z$ (corresponding to the lowest Landau subband) are given by[1]

$$|0, m\rangle = \frac{e^{ik_z z}}{\sqrt{2L}} \frac{(a^+)^m}{\sqrt{m!}} |0, 0\rangle \begin{bmatrix} 1 \\ 1 \end{bmatrix},\tag{4}$$

where m = 0, 1, . . . , ℓ; the ground (vacuum) state is

$$|0, 0\rangle = \frac{1}{l_H \sqrt{2\pi}} e^{-\frac{x^2+y^2}{4l_H^2}}.$$