

# Superconductivity and crystal structure of high-pressure phases in the niobium-ruthenium-hydrogen system

V. E. Antonov, T. E. Antonova, I. T. Belash, E. G. Ponyatovskii, and V. I. Rashchupkin

*Institute of Solid-State Physics, Academy of Sciences of the USSR, Chernogolovka, Moscow Province*

(Submitted September 5, 1986)

*Fiz. Tverd. Tela (Leningrad) 29, 1017-1025 (April 1987)*

Pressure dependences of the solubility of hydrogen in niobium-ruthenium alloys containing 17, 25.5, 31, and 50 at. % Ru at 325°C were obtained at hydrogen pressures up to 70 kbar, and an x-ray diffraction study was made of the crystal structure of the phases formed. The temperature  $T_c$  for the transition of these phases into the superconducting state in the range  $T \geq 2$  K was measured. In the  $Nb_{74.5}Ru_{25.5}-H$  and  $Nb_{69}Ru_{31}-H$  systems, there were phases with a hydrogen/metal atomic ratio  $n \approx 1$  and a tetragonally distorted fcc metal lattice, and with  $T_c \approx 5.1$  and 4.3 K, whereas the original niobium-ruthenium alloys showed no superconductivity for  $T \geq 2$  K.

It has been found<sup>1</sup> that electrolytic saturation of niobium-ruthenium alloys (20, 25, and 33 at. % Ru) with hydrogen considerably increases the transition temperature ( $T_c$ ) to the superconducting state, from  $\leq 0.25$  to 2-5 K. It was not possible to obtain reliable information about the crystal structure and the hydrogen content of the phases having these values of  $T_c$ , because the synthesized samples were not single-phase and were thermally unstable under normal conditions.

The mere detection of hydrides having  $T_c$  values higher than in the original materials is fairly significant; such hydrides have been synthesized, as regards bulk samples, only for the three metals palladium,<sup>2</sup> thorium,<sup>3</sup> and titanium,<sup>4</sup> and for three groups of niobium alloys: with ruthenium,<sup>1</sup> rhodium,<sup>5</sup> and palladium.<sup>5,6</sup> It was therefore useful to study the crystal structure, composition, and superconducting properties of niobium-ruthenium alloy hydrides by saturating with hydrogen at high pressure, the method which is at present surely the best for preparing bulk homogeneous single-phase hydride samples with a high chemical potential of the dissolved hydrogen.

One must acknowledge, however, that it was not always possible to obtain homogeneous single-phase samples of hydrides in the niobium-ruthenium-hydrogen system, even with high pressures of hydrogen. We therefore made a preliminary study of the phases formed at high pressures in the analogous tantalum-ruthenium-hydrogen<sup>7</sup> and vanadium-ruthenium-hydrogen<sup>8</sup> systems (which was in any case useful as regards the search for new superconducting hydrides), and only then proceeded to a more complete study of the niobium-ruthenium-hydrogen system.

Systems based on tantalum-ruthenium alloys<sup>7</sup> with 22.6 and 31 at. % Ru, and vanadium-ruthenium alloys<sup>8</sup> with 10, 18.5, and 34 at. % Ru, have been studied. For both of the tantalum alloys and for  $V_{90}Ru_{10}$ , superconducting hydrides were obtained with  $T_c \approx 3$  K and a hydrogen/metal atomic ratio  $n \approx 1$  based on close-packed metal lattices (orthorhombically distorted hcp for tantalum-ruthenium and fcc for  $V_{90}Ru_{10}$ ), whereas for all the initial alloys without hydrogen there was no superconductivity at  $T \geq 2$  K.

In the present paper, we report research on the niobium-ruthenium-hydrogen system based on niobium-ruthenium alloys with 17, 25.5, 31, and 50 at. % Ru.

## 1. SAMPLE PREPARATION AND EXPERIMENTAL METHOD

The alloys were prepared from 99.998% pure ruthenium powder ( $\sim 40$  mesh) and niobium purified by zone melting with resistance ratio  $R_{300} K/R_{4.2} K \approx 500$ . Alloy ingots were formed by fusion in an induction furnace in suspension in argon and annealed at 1200°C in a vacuum of  $\sim 10^{-6}$  torr for 24 h, then allowed to cool in the furnace. The samples were cut from the ingots by spark machining, a damaged surface layer  $\approx 0.05$  mm thick was ground off, and then a further layer of  $\approx 0.03$  mm was removed by electropolishing in sulfuric acid. The final dimensions of the samples were  $3 \times 3 \times 0.3$  mm. Chemical analysis with a CAMEBAX-MBX microanalyzer and a Link 860-500 energy dispersion x-ray spectrometer showed that the alloys did not change composition during melting and annealing within the error of measurement ( $\pm 0.4$  at. %), their ruthenium contents being 17, 25.5, 31, and 50 at. %.

The samples were hydrogenated by being held in an atmosphere of molecular hydrogen at 325°C with constant pressures up to 70 kbar for 24 h, followed by "quenching" under pressure to  $\approx 180^\circ C$ ; the procedure has been described,<sup>9</sup> and tests showed that there is almost no change in the hydrogen content and phase composition of the samples between 16 and 48 h. The error in the determination of the hydrogen pressure did not exceed 5%; the temperature was kept constant to within  $\pm 7^\circ C$ . To prevent loss of hydrogen from the prepared samples at atmospheric pressure, they were kept in liquid nitrogen.

At atmospheric pressure, the stability of the niobium-ruthenium-hydrogen samples with respect to disintegration into the metal and molecular hydrogen rapidly became less with increasing hydrogen content; for the samples with  $n \geq 1$ , a considerable amount of hydrogen was released within a few minutes at room temperature. There was, however, no complete release of hydrogen at room temperature over several days. After keeping in liquid nitrogen, there was no loss of hydrogen, at least over several months.

The hydrogen content in the samples was determined with relative error  $\pm 5\%$  from the amount of hydrogen evolved during thermal decomposition at up to 500°C; the method has been described.<sup>7</sup> The x-ray study was made photographically at 83 K

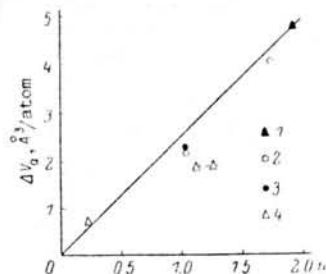


FIG. 1. Values of the volume increase  $\Delta V_a(n)$  per metal atom, plotted against the hydrogen content  $n$  for solid solutions of hydrogen in niobium-ruthenium alloys with (1) 17, (2) 25.5, (3) 31, and (4) 50 at.% Ru; continuous line, see text.

with a DRON-2.0 diffractometer, using  $\text{CuK}\alpha$  radiation; the samples were polycrystalline. The transition temperature to the superconducting state was found inductively for  $T \geq 2$  K;  $T_C$  was taken to be at half height of the step on the temperature dependence of the ac bridge imbalance signal.

## 2. EXPERIMENTAL RESULTS

Niobium-ruthenium alloys with 17, 25.5, and 31 at.% Ru should have<sup>10</sup> a bcc ( $\alpha$ ) structure, while that with 50 at.% Ru should have a structure that has not yet been interpreted but can be described on the basis of a face-centered orthorhombic (fcc) cell and will be denoted by  $\gamma''$ . The crystal structure types and parameters (see Table I, lines with  $n = 0$ ) for our alloys are in agreement with the earlier ones,<sup>10</sup> and for the 50 at.% Ru alloy there is good agreement with the whole set of diffraction lines reported.<sup>10</sup>

Estimates by Miedema's method<sup>11</sup> show that  $T_C$  for niobium-ruthenium alloys should decrease with increasing ruthenium content, to values not exceeding  $\sim 1.2, 0.15, 0.05, 0.03$  K for 17, 25.5, 31, and 50 at.% Ru respectively. The values found<sup>1</sup> for 20, 25, and 33 at.% Ru were 0.24, 0.25, and  $< 0.35$  K respectively. According to our results, none of the initial niobium-ruthenium alloys is superconducting for  $T \geq 2$  K.

The following facts concerning all niobium-ruthenium alloys are also important in the subsequent discussion. It is known<sup>12</sup> that for many transition metals and their alloys the dependences of the increase  $\Delta V_a(n) = V_a(n) - V_a(0)$  in the volume per metal atom on saturation with hydrogen are almost linear, and the slopes  $\beta = (\partial/\partial n)\Delta V_a(n)$  are quite similar. In particular,  $\Delta V_a(n)$  for all phases formed in the niobium-hydrogen system is satisfactorily expressed by a linear dependence with slope  $\beta \approx 2.5 \text{ \AA}^3/\text{H atom}$ .<sup>12</sup> It is seen from Fig. 1 that the same relation also gives a satisfactory description of  $\Delta V_a(n)$  for all the niobium-ruthenium-hydrogen phases obtained where the values were determinable, except for  $\text{Nb}_{50}\text{Ru}_{50}\text{-H}$  with  $n > 1$ . Consequently,  $\Delta V_a(n)$  with  $\beta = 2.5 \text{ \AA}^3/\text{H atom}$  was used here to estimate  $n$  from the results of structural studies of the niobium-ruthenium-hydrogen phases where the hydrogen content could not be determined experimentally.

We began the study of the phases formed in niobium-ruthenium-hydrogen systems at high pressures with hydrogen solutions in the 25.5 at.%

Ru alloy, whose composition lies approximately in the center of the content range for the niobium-ruthenium alloys hydrogenated in the previous work.<sup>1</sup>

## Solutions $\text{Nb}_{74.5}\text{Ru}_{25.5}\text{-H}$

The results are shown in Fig. 2 as dependences on the synthesis pressure of the hydrogen contents (Fig. 2a) and the x-ray results (Figs. 2c and 2d) shows that at pressures near  $P_{\text{H}_2} = 8$  kbar and at  $\approx 25\text{-}55$  kbar the system has phase transformations  $\alpha + \gamma'$  and  $\gamma' + \epsilon$  accompanied by the formation of hydride phases, respectively  $\gamma'$ -with a face-centered tetragonal (fct) and  $\epsilon$  with an hcp metal lattice. The hydrogen content in the  $\alpha$  solutions (based on the original bcc lattice of the alloy) reaches  $n \approx 0.05$  for  $P_{\text{H}_2} = 3$  kbar, and it follows from the values of  $\Delta V_a$  given in Fig. 2c that  $n$  scarcely increases in the two-phase ( $\alpha + \gamma'$ ) samples up to the pressure where the  $\gamma'$  phase extends throughout the volume. The mean hydrogen content in single-phase  $\gamma'$  samples prepared with  $10 \leq P_{\text{H}_2} \leq 20$  kbar is  $n = 1.04$ . From the constancy of  $\Delta V_a$  for the  $\gamma'$  phase (Fig. 2c), we can assume that the hydrogen content remains approximately the same in the two-phase ( $\alpha + \gamma'$ ,  $\gamma' + \epsilon$ ) samples. The  $\Delta V_a$  values for the  $\epsilon$  phase also vary only slightly throughout the range of formation of this phase at high hydrogen pressures; in the single-phase samples synthesized at  $P_{\text{H}_2} > 60$  kbar,  $n = 1.72$ .

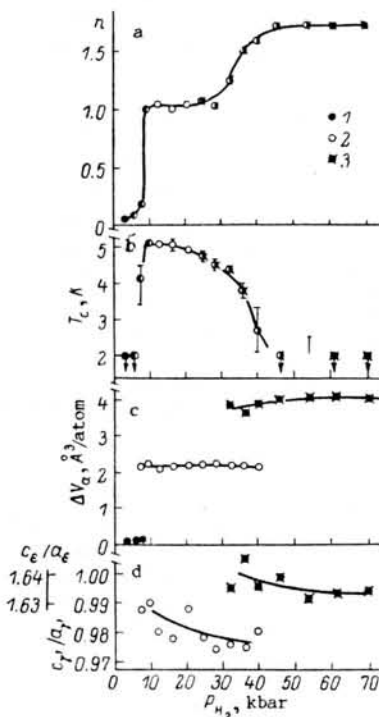


FIG. 2. Values of the hydrogen content  $n$  (a), the superconducting transition temperature  $T_C$  (b), the volume increase  $\Delta V_a$  per metal atom (c), and the ratio  $c/a$  for the fct and hcp metal sublattices in the  $\gamma'$  and  $\epsilon$  phases (d) for  $\text{Nb}_{74.5}\text{Ru}_{25.5}\text{-H}$  solid solutions obtained by heating at  $325^\circ\text{C}$  for 24 h with the hydrogen pressures shown as the abscissae; 1) results for  $\alpha$  solutions, 2) for  $\gamma'$  solutions, 3) for  $\epsilon$  solutions. The black-and-white symbols represent two-phase samples. The arrows with the symbols in Fig. 2b show that the samples were not superconducting for  $T \geq 2$  K; for the others, the temperature ranges of the superconducting transition are given.

TABLE I. Composition, Superconducting Transition Temperature, Formation Pressure at 325°C, Structure, and Metal Sublattice Parameters at Atmospheric Pressure and 83 K for Niobium-Ruthenium-Hydrogen Solid Solutions

at. % Ru	n	T <sub>c</sub> , K	$\nu_{H_2}$ , kbar	Structure	a, Å	b, Å	c, Å	c/a	a/c	b/c	V <sub>a</sub> , Å <sup>3</sup> /atom
17	0	< 2	—	$\alpha$	3.242	—	—	—	—	—	17.04
	?	~2.5 (?)	15...35	$\epsilon$	3.067	—	5.128	1.672	—	—	20.89
	1.92	< 2	≥40	$\epsilon'$	5.391	5.113	3.170	—	0.982 $\sqrt{3}$	1.613	21.84
25.5	0	< 2	—	$\alpha$	3.217	—	—	—	—	—	16.65
	1.04	5.08	12	$\gamma'$	4.244	—	4.180	0.985	—	—	18.82
	1.72	< 2	70	$\epsilon$	3.082	—	5.033	1.633	—	—	20.70
					(5.338)	(5.033)	(3.082)	—	( $\sqrt{3}$ )	(1.633)	(20.70)
31	0	< 2	—	$\alpha$	3.199	—	—	—	—	—	16.37
	1.04	≈4.3	20	$\gamma'$	4.23	—	4.16	0.98	—	—	18.6
	≥1.5	?	70	$\epsilon$	3.05	—	4.98	1.63	—	—	20.1
					(5.28)	(4.98)	(3.05)	—	( $\sqrt{3}$ )	(1.63)	(20.1)
50	0	< 2	—	$\gamma''$	4.371	4.225	3.396	—	1.287	1.244	15.68
	0.24	< 2	10...14	$\gamma''$	4.379	4.327	3.459	—	1.266	1.251	16.39
	1.13...1.25	< 2	22...70	$\epsilon'$	5.098	4.727	2.914	—	1.010 $\sqrt{3}$	1.622	17.56

Note.  $\alpha$  = bcc ( $V_a = a^3/2$ );  $\epsilon$  = hcp ( $V_a = (\sqrt{3}/2)a^2c$ );  $\epsilon'$  = orthorhombically distorted hcp ( $V_a = abc/4$ );  $\gamma'$  = fct,  $V_a = a^2c/4$ ;  $\gamma''$  = based on fcc pseudo-cell,  $V_a = abc/4$ . For the  $\epsilon$  solutions of hydrogen in alloys with 25.5 and 31 at.% Ru, the hcp lattice parameters in orthorhombic axes are shown in brackets.

The results of determining  $T_c$  for Nb<sub>74.5</sub>Ru<sub>25.5</sub>-H samples are shown in Fig. 2b. It is seen that values  $T_c \geq 2$  K were observed only in samples containing the  $\gamma'$  phase; the highest  $T_c \approx 5$  K occurred in single-phase  $\gamma'$  samples, and in the two-phase samples  $T_c$  decreased steadily with decreasing  $\gamma'$  phase content.

The results of the x-ray measurements suggest the hypothesis that in ( $\gamma' + \epsilon$ ) mixtures the decrease from the  $\gamma'$  phase  $T_c$  is due to the buildup of stacking faults. As the  $\epsilon$  phase content increases, the  $\gamma'$  phase diffraction lines rapidly become broader to such an extent that the splitting of the reflections by the tetragonal distortion of the fcc lattice for this phase becomes blurred. The  $\epsilon$  phase lines in such samples are also very broad; (220) and (311) of the  $\gamma'$  phase, and correspondingly (11.0) and (11.2) of the  $\epsilon$  phase, are joined by a high background level. These pairs of lines belong to reflections from just the systems of planes that are transformed into one another when the sequence of close-packed atomic layers changes from ABCABC... for the fcc lattice to ABABAB... for hcp; for fcc and hcp packings of spheres with equal radius, the respective interplanar distances are unchanged. If we assume that the  $\gamma' \rightarrow \epsilon$  transition in the Nb<sub>74.5</sub>Ru<sub>25.5</sub>-H system takes place by the accumulation of hcp stacking faults in the  $\gamma'$  phase, we should expect a local increase in the hydrogen concentration where such defects accumulate, since for a given hydrogen pressure the hydrogen solubility is seen from Fig. 2 to be greater in the hcp lattice phase. Increasing the hydrogen content causes a local dilatation of the metallic lattice of the alloy, and this increases the fraction of scattered radiation in the angle ranges between the lines (220) $\gamma'$ , (11.0) $\epsilon$  and (311) $\gamma'$ , (11.2) $\epsilon$ . The gradual accumulation of structural changes in the  $\gamma'$  phase with increasing  $\epsilon$  phase content in the samples also points to a change in the ratio  $c_{\gamma'}/a_{\gamma'}$  (Fig. 2d).

The presence of a considerable number of

stacking faults in the  $\gamma'$  and  $\epsilon$  phases may serve to explain also the very wide range of pressures at which the  $\gamma' \rightarrow \epsilon$  transition occurs, since with increasing stacking fault content the difference between the free energies of these phases becomes less.

From the above discussion, we can reasonably attribute to the  $\gamma'$  phase in the Nb<sub>74.5</sub>Ru<sub>25.5</sub>-H system the maximum value  $T_c = 5.08$  K which occurs in single-phase  $\gamma'$  samples, and this value is shown in Table I.

In order to establish how an increase in the ruthenium content alloyed with niobium affects the properties of the  $\gamma'$  phase, we studied the Nb<sub>69</sub>Ru<sub>31</sub>-H system; the value of  $T_c$  for a sample<sup>1</sup> got by hydrogenating Nb<sub>67</sub>Ru<sub>33</sub> was only  $\approx 2$  K, and we chose an alloy having a somewhat lower ruthenium content.

#### Solutions Nb<sub>69</sub>Ru<sub>31</sub>-H

Figure 3 and Table I show the results. The differences in properties between this system and Nb<sub>74.5</sub>Ru<sub>25.5</sub>-H are seen to be no more than quantitative. In particular, the maximum attainable hydrogen content in the  $\alpha$  solutions decreased to  $n \approx 0.03$ ; the  $\alpha \rightarrow \gamma'$  transition pressure and the hydrogen content in the  $\gamma'$  phase were almost unchanged; the  $\gamma' \rightarrow \epsilon$  transition range became wider and moved toward higher pressures. The  $T_c$  values for the single-phase  $\gamma'$  samples fell to  $\approx 4.3$  K. It was not possible to obtain single-phase  $\epsilon'$  samples, and the question of the  $\epsilon'$  superconducting properties thus remains unresolved. From the steady and gradual change in  $T_c$  for samples containing the  $\gamma'$  phase as the synthesis pressure increases (Fig. 3b), we can suppose that it is  $\gamma'$  which is superconducting in two-phase ( $\gamma' + \epsilon$ ) mixtures.

An estimate of the hydrogen content in the  $\epsilon$  phase, based on  $\Delta V_a$  (see Table I), gives  $n \approx \Delta V_a/\beta = (20.1-16.37)/2.5 \approx 1.5$ . This is close to

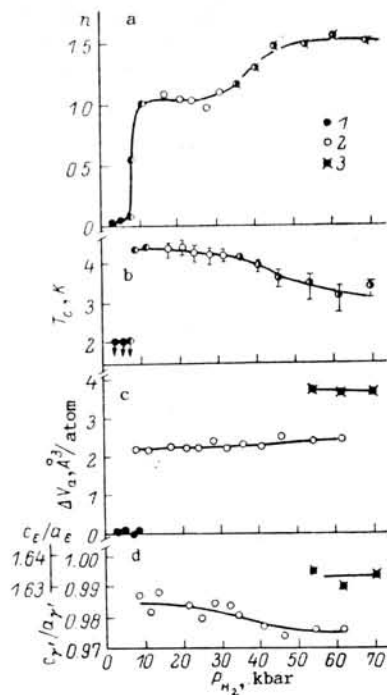


FIG. 3. Results of investigation of  $\text{Nb}_{69}\text{Ru}_{31}\text{-H}$  solid solutions; notation as in Fig. 2.

the value observed for two-phase ( $\gamma' + \epsilon$ ) samples formed with  $P_{\text{H}_2} \geq 55$  kbar (Fig. 3a), which according to the x-ray results contained only traces of the  $\gamma'$  phase. We may therefore suppose that the hydrogen content in the  $\epsilon$  phase of the  $\text{Nb}_{69}\text{Ru}_{31}\text{-H}$  system is in  $\approx 1.5$ , i.e., less than in that of the  $\text{Nb}_{74.5}\text{Ru}_{25.5}\text{-H}$  system.

Superconductivity was found<sup>7</sup> in tantalum-ruthenium-hydrogen solutions with an hcp (orthorhombically distorted) metal lattice and  $n \approx 1$ . It was possible to obtain a phase based on the hcp metal lattice with about the same hydrogen content in the niobium-ruthenium-hydrogen system also by taking alloys with a higher ruthenium content; for this purpose the  $\text{Nb}_{50}\text{Ru}_{50}$  alloy was chosen; the results regarding the phase composition of niobium-ruthenium alloys with a higher ruthenium content are contradictory.<sup>1,3</sup>

#### Solutions $\text{Nb}_{50}\text{Ru}_{50}\text{-H}$

The results are shown in Fig. 4 and Table I. It is seen from the diagram that at 325°C increasing the hydrogen pressure to  $\approx 8$  kbar raises the hydrogen content in solutions based on the original  $\gamma''$  structure of the  $\text{Nb}_{50}\text{Ru}_{50}$  alloy ( $\gamma''_1$  solutions) to  $n \approx 0.01$ . For  $P_{\text{H}_2} \approx 8\text{-}10$  kbar, the phase transition  $\gamma''_1 \rightarrow \gamma''_2$  occurs, accompanied by a discontinuous increase in the hydrogen content of the alloy to  $n \approx 0.24$ . The  $\gamma''_2$  phase, like  $\gamma''_1$ , is a solution of hydrogen based on the  $\gamma''$  structure of  $\text{Nb}_{50}\text{Ru}_{50}$ , but with higher values of the fcc pseudocell parameters and a change in their ratios. At pressures from  $\approx 15$  to  $\approx 20$  kbar, there is a further phase transition, and the  $\epsilon'$  phase is formed with an orthorhombically distorted hcp metal lattice. The hydrogen content in the  $\epsilon'$  phase increases from  $n \approx 1.13$  to  $n \approx 1.25$  as the synthesis pressure rises from  $\approx 20$  to 70 kbar, but this is, within the error measurement, not ac-

companied by any change  $\Delta V_a$  or any change in the ratios of the metal lattice parameters of the phase.

The hydrogen contents in the  $\epsilon'$  phase and the amount of orthorhombic distortion of its hcp metal sublattice, represented by the deviation of  $a_{\epsilon'}/c_{\epsilon'}$  from  $\sqrt{3}$ , are close to those observed for the superconducting  $\epsilon'$  phases in the analogous tantalum-ruthenium-hydrogen system, but no superconductivity was found in the  $\text{Nb}_{50}\text{Ru}_{50}\text{-H}$   $\epsilon'$  solutions at  $T \geq 2$  K. Nor were  $\gamma''_1$  and  $\gamma''_2$  solutions formed.

Our next step was to ascertain whether it is possible to obtain phases with high  $T_c$  by hydrogenation of niobium-ruthenium alloys having a lower ruthenium content than before.<sup>1</sup>

#### Solutions $\text{Nb}_{83}\text{Ru}_{17}\text{-H}$

The results of the measurements are shown in Fig. 5 and Table I. It was possible to obtain single-phase samples in the  $\text{Nb}_{83}\text{Ru}_{17}\text{-H}$  system only at pressures above  $\approx 40$  kbar. Under these conditions,  $\epsilon'$  solutions with  $n \approx 1.9$  and an orthorhombically distorted hcp metal sublattice were formed, whose parameters (Table I) were independent of the synthesis pressure within the experimental error.

No samples obtained with  $P_{\text{H}_2} < 40$  kbar were single-phase, nor were they made so by either extending to 48 h the time under high pressure of hydrogen or raising the holding temperature from 250 to 350°C.

Samples synthesized with  $P_{\text{H}_2} \leq 12$  kbar consisted of a mixture of phases with a wide range of lattice parameters, indicating an inhomogeneous distribution of hydrogen within them. With in-

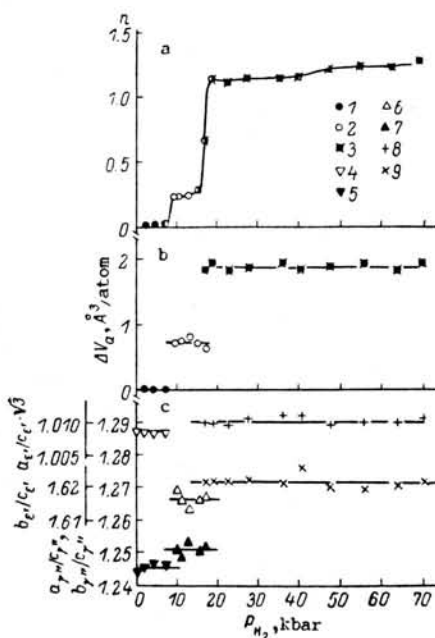


FIG. 4. Values of the hydrogen content  $n$  (a), the volume increase  $\Delta V_a$  per metal atom (b), and the ratio of metal sublattice parameters (c) for  $\text{Nb}_{50}\text{Ru}_{50}\text{-H}$  solutions obtained by heating at 325°C for 24 h with the hydrogen pressures shown as the abscissae; 1)  $n$  and  $\Delta V_a$  for  $\gamma''_1$  solutions, 2) for  $\gamma''_2$  solutions, 3) for  $\epsilon'$  solutions; 4, 5)  $a_{\gamma''}/c_{\gamma''}$  and  $b_{\gamma''}/c_{\gamma''}$  for  $\gamma''_1$  solutions, 6, 7) for  $\gamma''_2$  solutions; 8, 9)  $a_{\epsilon'}/c_{\epsilon'}$  and  $b_{\epsilon'}/c_{\epsilon'}$  for  $\epsilon'$  solutions.

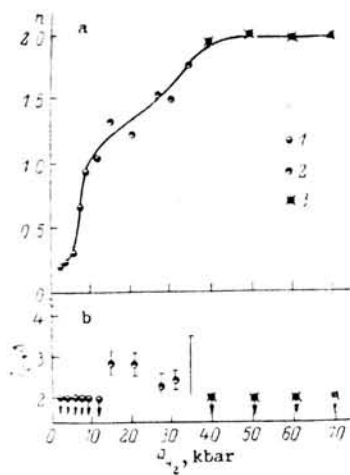


FIG. 5. Values of the hydrogen content  $n$  (a) and the superconducting transition temperature  $T_c$  (b) for  $Nb_{83}Ru_{17}-H$  solutions obtained by heating at  $325^\circ C$  for 24 h with the hydrogen pressures shown as the abscissae; 1) results for samples consisting of a mixture of  $\alpha$  phases; 2) for samples containing the  $\epsilon$  phase; 3) for  $\epsilon'$  samples. Other notation in Fig. 5b is as in Fig. 2b.

creasing synthesis pressure, the  $\alpha$  phase parameters increased and their spread became less for each sample. A fairly homogeneous  $\alpha$  phase sample, having  $a = 3.396 \text{ \AA}$  close to the maximum was obtained with  $P_{H_2} = 12 \text{ kbar}$ . The value  $n = \Delta V_a/\beta \approx 1$  for this sample, estimated from that of  $\Delta V_a$ , is in good agreement with experiment (Fig. 5a).

In the pressure range from  $\approx 15$  to  $\approx 35 \text{ kbar}$ , samples were obtained which consisted of a mixture of at least three phases. a) A new  $\epsilon$  phase with an hcp metal sublattice, occurring to the greatest extent in samples synthesized at pressures near the middle of the range mentioned. The lattice parameter values for this phase depended only slightly on the synthesis pressure; Table I gives average values. The value of  $\Delta V_a$  for the  $\epsilon$  phase corresponds to a hydrogen content  $n = \Delta V_a/\beta = (20.89-17.04)/2.5 \approx 1.5$ . b) An  $\alpha$  phase whose lattice parameter corresponds to  $n \approx 1$  or somewhat less. The content of this phase in the samples decreased rapidly with increasing synthesis pressure. c) An  $\epsilon'$  phase with about the same lattice parameters as in single-phase  $\epsilon'$  samples formed at higher hydrogen pressures. The content of the  $\epsilon'$  phase in the samples increased with the synthesis pressure.

It is seen from Fig. 5b that in the  $Nb_{83}Ru_{17}-H$  system only the samples containing the  $\epsilon$  phase were superconducting at  $T \geq 2 \text{ K}$ . According to the foregoing results, it would be reasonable to attribute to that phase the observed  $T_c$  values, as has been done in Table I. Here, however, it should be noted that the diffraction patterns of the majority of samples containing the  $\epsilon$  phase showed quite clearly, in addition to the  $\alpha$ ,  $\epsilon$ , and  $\epsilon'$  phase lines a further unidentified line corresponding to an interplanar distance  $d \approx 2.30-2.31 \text{ \AA}$ . It is therefore possible that the mixtures studied contained also a fourth phase which was the superconducting one.

### 3. DISCUSSION OF RESULTS

The properties studied here can be regarded

as reliably determined for superconducting hydride in two systems:  $Nb_{74.5}Ru_{25.5}-H$  and  $Nb_{69}Ru_{31}-H$ . These are  $\gamma'$  phases with  $n = 1.04 \pm 0.05$ , a tetragonally distorted fcc metal lattice, and  $T_c$  values of 5.08 and 4.3 K (see Table I). The  $T_c$  values in the  $\gamma'$  phases are in satisfactory agreement with previous ones<sup>1</sup> for electrolytically hydrogen-saturated niobium-ruthenium alloys containing 20, 25, and 33 at. % Ru. However, the conclusions drawn<sup>1</sup> regarding the crystal structure of the superconducting phases differ from ours, and it is necessary to discuss this discrepancy.

Only a single x-ray picture was taken<sup>1</sup> of the superconducting  $Nb_{80}Ru_{20}-H$  sample; while being put into the x-ray cryostat, the sample was at room temperature for several minutes. The diffraction pattern showed five very broad lines; four of these were attributed to an fcc phase with  $a = 4.41 \text{ \AA}$  ( $\Delta V_a \approx 4.81 \text{ \AA}^3/\text{atom}$ ), and the fifth to a bcc phase with  $a \approx 3.32 \text{ \AA}$  ( $\Delta V_a \approx 1.67 \text{ \AA}^3/\text{atom}$ ). The fcc phase was taken to be the superconducting one.

According to the  $\Delta V_a$  value, this fcc phase should be a dihydride of  $Nb_{80}Ru_{20}$  ( $n \sim \Delta V_a/\beta \approx 1.9$ ). It is, however, entirely probable that the phase is not a hydride at all. Firstly, according to our estimates, during the few minutes that the  $Nb_{80}Ru_{20}-H$  sample was at room temperature, a phase with such a high content of hydrogen must necessarily have dissociated. Secondly, we have found that a phase with an fcc lattice (probably a carbide) up to  $\sim 0.03 \text{ mm}$  deep is formed in the surface layer when niobium-ruthenium alloys undergo spark machining. The lattice parameter of this phase is unchanged by hydrogenation of the samples; interpolation to the composition  $Nb_{80}Ru_{20}$  gives  $a \approx 4.43 \text{ \AA}$  for it, which is close to the value  $a \approx 4.41 \text{ \AA}$  for the fcc phase.<sup>1</sup> The sample<sup>1</sup> was cut by spark machining. Thus, the interpretation<sup>1</sup> of the structural results appears unconvincing.

From our results, in all three analog systems studied (tantalum, vanadium, and niobium with ruthenium and hydrogen), hydrides with  $n \geq 1$  are formed on the basis of close-packed metal lattices; those with  $n \approx 1$  are superconductors, those with  $n > 1$  are not. The difference between these hydrides may be that in phases with  $n \approx 1$  the hydrogen atoms occupy octahedral interstitial positions in the metal lattice (in close-packed lattices, there is one octahedral pore per lattice site); in those with  $n > 1$ , they occupy tetrahedral ones (of which there are two per site). In the close-packed superconducting palladium hydride lattice, the hydrogen is indeed in octahedral pores,<sup>14</sup> and, of the two new intermediate phases found<sup>4</sup> in the titanium-hydrogen system, for the same hydrogen content  $n = 0.71$ , the superconducting phase was the one with the hydrogen in octahedral pores, whereas the one with it in tetrahedral pores did not possess superconductivity.<sup>15</sup> This may occur because in all the superconducting hydrides studied, as in palladium hydride, an important contribution to the electron-phonon interaction constant comes from the interaction of electrons with optical vibrations of hydrogen atoms, and the vibration frequencies in octahedral pores are considerably lower than in tetrahedral pores.<sup>14</sup>

We would also point out the following in connection with the type of position occupied by interstitial hydrogen in niobium-ruthenium-hydrogen

alloys with  $n > 1$ . Tetrahedral coordination of hydrogen is characteristic of all known dihydrides of transition metals.<sup>16</sup> It is unlikely that the  $\epsilon'$  phase dihydride of  $Nb_{83}Ru_{17}$  forms an exception. Phases with  $n > 1$  based on other alloys may be regarded as modifications of this  $\epsilon'$  phase, whose properties vary smoothly as the ruthenium content increases. It is seen from Table I that  $n$  and  $\Delta V_a$  for such phases decrease steadily, while the ratio  $a/c$  (in terms of orthorhombic axes) increases from  $a/c < \sqrt{3}$  for an alloy with 17 at.% Ru to  $a/c \approx \sqrt{3}$  for those with 25.5 and 31 at.% (for  $a/c = \sqrt{3}$ , the lattice reaches hexagonal symmetry) and  $a/c > \sqrt{3}$  for that with 50 at.% Ru. It is reasonable to suppose that the hydrogen coordination remains tetrahedral in all these phases.

This discussion of the hydrogen coordination in hydrides requires direct experimental verification, of course. Work on this has started.

<sup>1</sup>C. G. Robbins, M. Ishikawa, A. Treyvaud, and J. Muller, *Solid State Commun.* **17**, 903 (1975).

<sup>2</sup>T. Skośkiewicz, *Phys. Status Solidi A* **11**, K123 (1972).

<sup>3</sup>C. B. Satterthwaite and D. T. Peterson, *J. Less-Common Met.* **26**, 361 (1972).

<sup>4</sup>E. G. Ponyatovskii, I. O. Bashkin, V. F. Degtyareva, V. I. Rashchupkin, O. I. Barkalov, and Yu. A. Aksenov, *Fiz. Tverd. Tela (Leningrad)* **27**, 3446 (1985) [*Sov. Phys. Solid State* **27**, 2077 (1985)].

<sup>5</sup>H. Oesterreicher and J. Clinton, *J. Solid State Chem.* **17**, 443 (1976).

<sup>6</sup>C. G. Robbins and J. Muller, *J. Less-Common Met.* **42**, 19 (1975).

<sup>7</sup>V. E. Antonov, T. E. Antonova, I. T. Belash, V. Yu. Malyshev, E. G. Ponyatovskii, and V. I. Rashchupkin, *Fiz. Tverd. Tela (Leningrad)* **28**, 2352 (1986) [*Sov. Phys. Solid State* **28**, 1316 (1986)].

<sup>8</sup>V. E. Antonov, I. T. Belash, E. G. Ponyatovskii, V. I. Rashchupkin, and I. M. Romanenko, *Fiz. Tverd. Tela (Leningrad)* **29**, 665 (1987) [*Sov. Phys. Solid State* **29**, 381 (1987)].

<sup>9</sup>E. G. Ponyatovskii, V. E. Antonov, and I. T. Belash, *Usp. Fiz. Nauk* **137**, 663 (1982) [*Sov. Phys. Usp.* **25**, 596 (1982)].

<sup>10</sup>E. Raub and W. Fritzsche, *Z. Metallkd.* **54**, 317 (1963).

<sup>11</sup>A. R. Miedema, *J. Phys. F* **4**, 120 (1974).

<sup>12</sup>H. Peisl, in: *Hydrogen in Metals I* (ed. by G. Alefeld and J. Völkl), Springer Verlag, Berlin (1978), p. 53.

<sup>13</sup>F. A. Shunk, *Second Suppl. to M. Hansen and K. Anderko, Constitution of Binary Alloys*, McGraw-Hill, New York (1969).

<sup>14</sup>T. Springer, in: *Hydrogen in Metals I* (ed. by G. Alefeld and J. Völkl), Springer Verlag, Berlin (1978), p. 75.

<sup>15</sup>A. I. Kolesnikov, V. K. Fedotov, I. Natkaniec, S. Khabrylo, I. O. Bashkin, and E. G. Ponyatovskii, *Pis'ma Zh. Eksp. Teor. Fiz.* **44**, 396 (1986) [*JETP Lett.* **44**, 509 (1986)].

<sup>16</sup>M. M. Antonova, *Properties of Metal Hydrides* [in Russian], Naukova Dumka, Kiev (1975).

Translated by J. B. Sykes

## Radiative transitions between anion and cation valence bands in CsBr crystals

Yu. M. Aleksandrov, I. L. Kuusmann, P. Kh. Liblik, Ch. B. Lushchik, V. N. Makhov, T. I. Syreishchikova, and M. N. Yakimenko

*P. N. Lebedev Physics Institute, Academy of Sciences of the USSR, Moscow*

(Submitted September 5, 1986)

*Fiz. Tverd. Tela (Leningrad)* **29**, 1026-1029 (April 1987)

The excitation spectrum of the 6 eV luminescence of CsBr crystals was found to have a threshold energy of 13.5 eV, corresponding to the onset of photoionization of cesium ions. The luminescence was due to recombination of electrons from an anion valence band with holes self-localized at cations. Dissociation of cation excitons (13.2 eV) was accompanied by the creation of cation defects in CsBr and this was manifested in thermally stimulated luminescence.

Strong short-lived ( $\tau < 1$  nsec) intrinsic luminescence of  $BaF_2$  crystals excited beyond the threshold of the  $E_g^c$  transitions from the  $Ba^{2+}(5p)$  valence band to the conduction band ( $h\nu > E_g^c \approx 18$  eV), i.e., beyond the threshold of formation of holes in the  $Ba^{2+}(5p)$  band, is shown in Refs. 1-3 to be due to radiative transitions of electrons from the  $F^-(2p)$  anion valence band to the  $Ba^{2+}(5p)$  cation valence band of these crystals. It is demonstrated in Ref. 3 that a "strong" radiative decay channel of the same type as in  $BaF_2$  should occur also in other ionic crystals with a sufficiently low ionization energy  $E_g^c$  of the cations for which the width of the band gap  $E_g$  exceeds the energy separation between the anion and cation valence bands. In particular, this effect may occur in CsBr crystals.

Pure CsBr crystals emit not only luminescence bands due to anion self-localized excitons at 3.5 and 4.7 eV, but also cathodoluminescence bands<sup>4, 5</sup> observed at 80 K in the region of 5-6.2 eV. This luminescence is not excited in the region of the long-wavelength exciton absorption band (6.8 eV) and it cannot be attributed to the usual two-halogen excitons.

Figure 1 shows the luminescence spectra, recorded using apparatus with a double vacuum monochromator, of CsBr crystals excited by 6 keV electrons at 10 and 190 K. At 10 K there were four maxima at 5.00, 5.43, 5.80, and 6.2 eV. The cathodoluminescence intensity remained high up to 80 K, but thermal quenching occurred at higher temperatures. The cathodoluminescence of CsBr