Acoustic investigations of low-temperature phase transitions in Nb and V hydrides

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Hydrides of niobium and vanadium containing large amounts of hydrogen (H/Me > 0.7) are investigated by the method of low-frequency acoustics (1–6 kHz). At temperatures from 1.5 to 300 K, elastic-modulus and sound-damping anomalies corresponding to second-order phase transitions were observed. A comparison of the anomalies of the elastic modulus and of the thermal-expansion coefficient near the phase transition in $VH_{0.73}$ at $T_c = 201.5$ K has shown that a phase transition of the ordering type in a metallic system is described by the same thermodynamic relations as, e.g., the λ transition in heluim. In the Nb–H system at $T \sim 100$ K, a second-order phase-transition line was observed in the interval $0.82 \leq H/Nb \leq 0.93$. Regions of fluctuations of the order parameter are observed near the phase transitions in the hydrides of niobium and vanadium; the critical exponent β is close to 1/3. It appears that the investigated phase transitions are the first example of ordering-type transformations, in a metallic system, which display a critical behavior.

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INTRODUCTION

Transition-metal hydrides, which are interstitial alloys with large hydrogen content (H/Me ~ 1) have a number of unusual properties. This is due for the most part to the presence in the hydrides of two greatly differing subsystems, namely a metallic matrix and light hydrogen contained in its interstices and characterized by an anomalously high diffusion mobility ($D \sim 10^{-5}$ cm^2/sec at $T \sim 300$ K in Nb-H). The phase diagrams of the hydrides correspond topologically to the gas–liquid–solid diagrams of real gases.[1] The phases α and α' have respectively the properties of a lattice gas[2] and a lattice liquid, while in the "solid" β phase a sublattice consisting of hydrogen atoms is produced. The investigation of the structures of the hydrogen sublattices was initiated in Refs. 3 and 4 (see the review[5]), in which it was shown that the "hydrogen subcrystal" made up of the lattice liquid can become additionally ordered after cooling. This process consists, according to Ref. 6, of a number of steps, each of which is an ordering-type phase transition in a structure of hyper- or hypostoichiometric type (e.g., $MH_{0.5+x}$ or $MH_{0.5-x}$). Each degree of ordering leads to an increase of the parameters of the superstructure cells, and the entire process can thus be represented as a sequence of phase transitions in Ising lattices, with successively increasing steps.

Information on the low-temperature phases of the hydrides (produced during the second and higher degrees of ordering at $T < 200$ K) are most incomplete.[7–9] Even in those few cases when the structures of the low-temperature phases were determined, the character of the phase transitions is unknown.

It is obvious that to calculate the low-temperature phase transitions in Me-H systems it is reasonable to use, besides the neutron-diffraction method, also measurements of physical quantities that are directly connected with the thermodynamic functions of the system (velocity and damping of the sound, heat capacity, thermal-expansion coefficient). As early as in 1935 it was shown[10] that the connection between the equilibrium order parameter and the external elastic stress leads to the appearance of relaxation absorption of sound. A detailed theoretical investigation of this phenomenon was carried out in Refs. 11 and 12. At the present time, the acoustic method is quite widely used to investigate phase transtions in solids; in individual cases there is a well established connection between the static and dynamic characteristics of the transition, on the one hand, and the experimentally measured anomalies of the damping and speed of sound near T_c, on the other.[13,14]

In this study we have used the low-frequency acoustic method to study phase transitions in the hydrides of niobium and vanadium at $T < 250$ K.

2. EXPERIMENT

The measurements were performed with an elastic-relaxation spectrometer operating in the regenerative regime[15] in the frequency range 1–6 kHz. The samples were plates serving as quarter-wave and full-wave vibrators with transverse vibrations. During the time of the experiments, while the samples were slowly heated (0.05–0.2 deg/min), we measured the temperature dependences of the resonant frequency ν of the sample and of the logarithmic damping decrement δ. The damping of the sound is given henceforth in units of the reciprocal Q factor of the acoustic vibrator, $Q^{-1} = \delta/\pi$, and in place of the elastic modulus G we plot on the diagrams the square ν^2 of the resonant frequency of the sample (inasmuch as $\nu^2 \propto G$ for an acoustic vibrator).

To measure the thermal expansion we used a dilatometer in which the electromechanical converter was a 6MKh3S movable-electrode tube (Ref. 16) connected in a bridge circuit whose unbalance voltage was registered with a digital voltmeter ShCh1413. The sensitivity of the instrument was ~0.5 μm; the measurements were made while the sample was heated at a rate ~0.1 deg/min.

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The samples were made of niobium hydrides with H/Nb = 0.83–0.93 and vanadium hydrides with H/V = 0.73–0.75.

3. RESULTS

1. *The system* $NbH_{0.82}$–$NbH_{0.93}$. The temperature dependences of the elastic modulus and of the sound damping of single-crystal hydride with H/Nb = 0.83 in the temperature interval 1.5–230 K are shown in Fig. 1. As seen from the figure, three anomalies are observed on the elastic-modulus curve, at $T \sim 100$, ~190, and ~220 K; their character is such that they can be attributed to phase transitions.[13,14] In the temperature interval 1.5–100 K, the plot of the elastic-modulus decrease is similar to the Curie-Weiss curve. The transition at $T \sim 220$ K corresponds to an analogous dependence, but the curve is a mirror reflection about the abscissa axis. A situation in which the high-temperature phase has a larger elastic modulus than the low-temperature phase is not frequently encountered. The sound-damping curve also has three anomalies, two of which, at $T \sim 100$ and ~190 K, take the form of λ-like maxima, and the third, at $T \sim 220$ K is in the form of a kink.

The curves obtained for hydrides with other compositions (H/Nb = 0.82, 0.89, 0.93) exhibit anomalies similar to those shown in Fig. 1, but the corresponding phase-transition temperatures are somewhat displaced (their positions are shown on the phase diagram of Fig. 5).

To determine the character of the transitions, the anomalies of the elastic modulus near T_c were approximated by a power-law dependence. The best approximation of the quantity $(\Delta G/G)^n$ to a straight line as a function of temperature was reached at $n \approx 3$. Extrapolation of this line to $(\Delta G/G)^n = 0$ yielded more accurate values of the transition temperatures for the hydride $NbH_{0.83}$, $T_c = 100.2$ and 218.0 K. Figure 2 shows in a doubly logarithmic scale the plot of $\Delta G/G$ against $\varepsilon = (T_c - T)/T_c$ for the phase transition at $T_c = 100.2$ K. The value $\beta = 1/n$, obtained by least squares, and the temperature intervals in which the power-law approximation is valid, are given for both transitions in Table I. Since the phase-transition temperatures depend on the hydrogen content, the determination of T_c at the indicated accuracy is meaningful only for each individual sample for the purpose of obtaining exact values of ε.

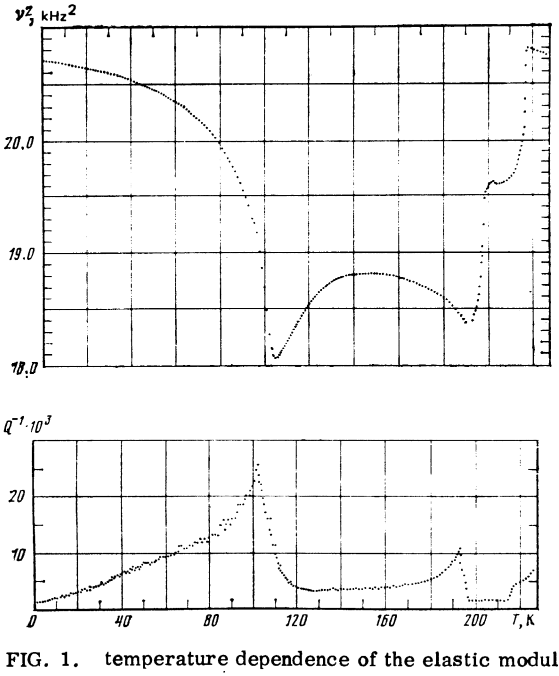

FIG. 1. temperature dependence of the elastic modulus and of the sound damping of the hydride $NbH_{0.83}$.

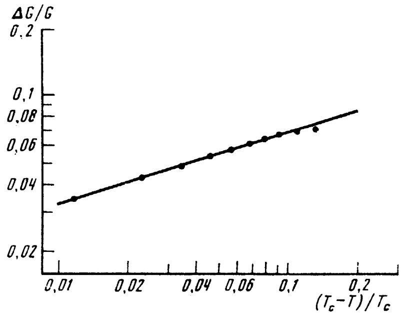

FIG. 2. Dependence of the elastic modulus on the temperature, in a doubly logarithmic scale, for the phase transition at $T_c = 100.2$ K in $NbH_{0.83}$.

It was noted in some papers that phase transitions of the ordering type in hydrides can become slowed down at low temperatures. For example, in the system V_4D_3, when cooled below 215 K, one observes first a metastable superstructure that is replaced by another as a result of being kept for a long time at liquid-nitrogen temperature.[17] In palladium hydride with H/Pd = 0.76, the ordering at 70 K lasts from 50 to 300 hours.[18] A check on the $NbH_{0.83}$ system revealed, within an accuracy limit 10^{-3}, that at 79 K there is no time dependence of the elastic modulus for 140 hours. This result, as well as the good reproducibility of the Q^{-1} and ν^2 curves when the sample heating rate is changed from 0.05 to 0.2 deg/min, shows that the obtained temperature dependences of the elastic modulus and of the sound damping are close to equilibrium (the temperature dependences of the relaxation time were not determined separately).

2. *The systems* $VH_{0.73}$–$VH_{0.75}$. The dependences of the elastic modulus and of the sound damping of vanadium hydrides with H/V = 0.73–0.75 were plotted in the temperature interval 80–300 K. Figure 3 shows plots typical of the indicated ratios. As seen from the figure, the elastic-modulus anomaly due to the phase transition at $T \sim 200$ K is of the same form as in the case of the phase transition at 100.2 K in $NbH_{0.85}$, but is stretched out in comparison with the latter. The dif-

TABLE I.

System	T_c, K	β	Interval of
$NbH_{0.83}$	100.2	0.339±0.009	$1.7\cdot10^{-2}<\varepsilon<2.5\cdot10^{-1}$
$NbH_{0.83}$	218.0	0.328±0.004	$6.9\cdot10^{-3}<\varepsilon<3.0\cdot10^{-2}$
$VH_{0.73}$	201.5	0.326±0.007	$3.5\cdot10^{-2}<\varepsilon<3.7\cdot10^{-1}$

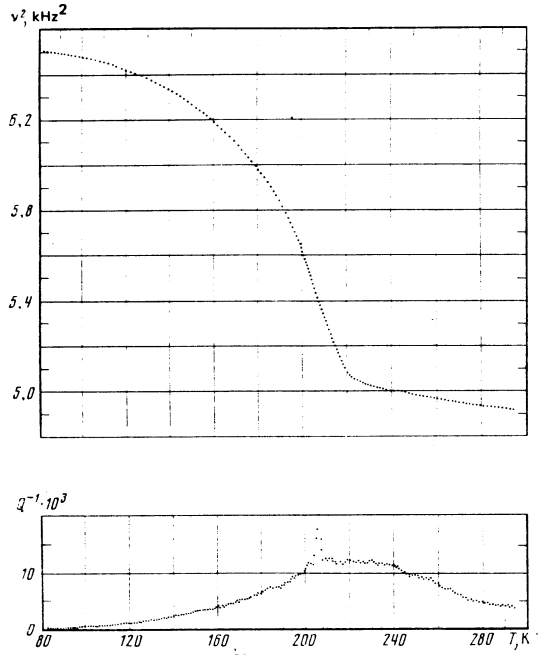

FIG. 3. Temperature dependence of the elastic modulus and of the sound damping of the hydride $VH_{0.73}$.

ference in the damping maximum consists of a more gently sloping high-temperature branch; in addition, a sharp burst is observed at $T = 203$ K.

It was observed that, just as for the phase transitions in $NbH_{0.83}$, the temperature dependence of the elastic modulus near T_c can be approximated by a power-law function. In similar fashion, a more accurate value $T_c = 201.5$ K and an exponent $\beta = 1/n$ close to 1/3 were obtained (see Table I).

In addition to the acoustic measurements on the vanadium hydrides, measurements were made of the thermal expansion $\Delta l(T)$ in the temperature range 80–250 K. The results of the measurements for the hydride with H/V = 0.73 are shown in Fig. 4. As seen from the figure, near the phase transition at $T_c = 201.5$ K, a λ-shaped anomaly of the thermal-expansion coefficient α is observed. This shape of the α curve is in agreement with the results of theoretical calculations.[19] A λ-shaped anomaly of the coefficient of thermal expansion was observed experimentally, for example, upon ordering of the alloy Cu_3Au.[20,21]

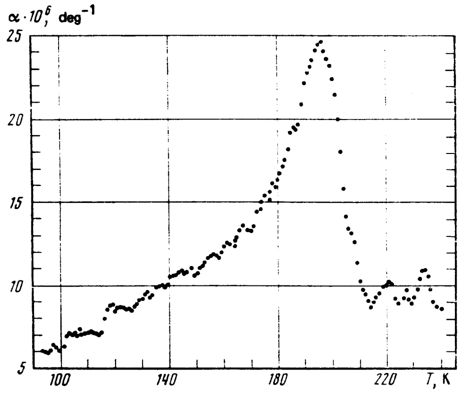

FIG. 4. Temperature dependence of the coefficient of thermal expansion of the hydride $VH_{0.73}$.

4. DISCUSSION OF RESULTS

1. *Phase diagrams and structure of low-temperature phases*. Figure 5 shows the low-temperature region of the phase diagram of the Nb-H system, which includes the hydrogen-concentration interval used in the present study. The dark squares in this figure represent the second-order phase-transition points obtained for hydrides with four compositions. The anomalies of the elastic modulus and sound damping in all these cases had the same character as at H/Nb = 0.83 (Fig. 7). The dark triangles represent anomalies of a substantially different character (jumplike change of the modulus and narrow damping maxima). The light circles in Fig. 5 are the results of an investigation of the Nb-H system by the method of differential thermal analysis.[22] According to these data, a λ phase is produced at $T < 240$ K, but its structure, as well as the character of the phase transitions, have not been determined. In the only published structural investigation of niobium hydride with a composition close to that used in the present study ($NbH_{0.83}$), a long-period structure was observed at $T < 250$ K, with a unit cell approximately 14 times larger than the unit cell of the metal,[23] but the structure of the phase was not determined, owing to the limited number of observed reflections. The solid line in the figure shows the γ-phase region observed in Ref. 24 by the diffraction method.

It is seen from Fig. 5 that the second-order phase-transition temperatures observed by the acoustic method near 200 K (Ref. 25) agree with the results of Ref. 22. The anomalies, which constitute jumplike changes of the elastic modulus and narrow damping maxima, as seen from the figure, lie on the line that separates the phases $\beta - (\gamma + \beta)$ and $(\gamma + \beta) - \gamma$.

The phase transitions at $T \sim 100$ K, observed in the present study for all the investigated compositions of the hydrides, were not observed previously. It can be concluded from the results that a line of second-order phase transitions is present in the investigated concentration region at $T \sim 100$ K.

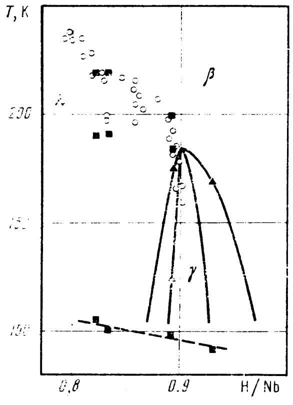

FIG. 5. Low-temperature part of the Nb-H phase diagram.

In contrast to the Nb-H system, for which the structures of the low-temperature phases are unknown, for vanadium hydrides the situation is different in the investigated region of the phase diagram. In Refs. 26–29, using calorimetric, resistance, and diffraction measurements, it was shown that, at $0.5 < H/V < 0.75$ and $T < 200$ K, a δ phase with a stoichiometry V_3H_2 is produced.[27] The unit cell of the low-temperature δ phase with parameters $a = (a_0^2 + c_0^2)^{1/2}$, $b = a_0$, and $c = (4a_0^2 + c_0^2)^{1/2}$ (a_0 and c_0 are the parameters of the tetragonal cell of the initial β phase) along the [101] direction is three times larger than the unit cell of the β phase. This transition fits well the steplike ordering model. The good agreement between the phase-transition temperatures obtained in the present paper and the results of Refs. 26–29 shows that the observed anomalies of the elastic modulus, of the sound damping, and of the thermal-expansion coefficient are connected with formation of the δ phase.

2. *Use of the Pippard relations*. In an investigation of the structure of phase transitions in the solid phase, such factors as the anisotropic striction, internal inhomogeneities, domain structure, etc. can lead to a distortion of the simple relations that connect, e.g., the order parameter with the elastic modulus or with the coefficient of thermal expansion. It is possible, however, to verify the internal consistency of the results of measurements of different physical quantities near the transition temperature and to estimate the degree of influence of the indicated factors, by using Pippard's relations,[30] which connect the thermodynamic quantities near the λ point:

$$C_p = T(dp/dT)_\lambda \alpha_p + \text{const}, \tag{1}$$

$$\alpha_p = (dp/dT)_\lambda \beta^T + \text{const} \tag{2}$$

[here C_p is the heat capacity, α_p is the coefficient of thermal expansion, β^T is the isothermal compressibility, and $(dp/dT)_\lambda$ is the reciprocal of the change of the transition temperature with changing pressure].

These relations were first derived phenomenologically.[30] In Ref. 31, however, exact thermodynamic relations between C_p, α_p, and β^T were obtained for the λ transition in helium, and turned out to be equivalent to the Pippard relations in the asymptotic case of proximity to the λ line. In Ref. 32, a generalization of (1) and (2) in tensor form was presented for the stress-strain variables, and in Ref. 33, for variables describing phase transitions in ferroelectrics. It should be noted that expressions (1) and (2) correspond to the known Ehrenfest relations[34] that relate, at the second-order phase-transition point, the discontinuities of the heat capacity, the coefficient of thermal expansion, and the compressibility. Unlike the Ehrenfest relations, however, the Pippard relations connect the same quantities in a certain region near the transition temperature.

The validity of (1) and (2) was experimentally confirmed for the λ point in helium-4 (Refs. 33 and 35) and for phase transitions in ammonium chloride,[30,36] quartz,[37] and triglycin sulfate.[33] Figure 6 shows the dependence of the reciprocal of the elastic modulus on the thermal-expansion coefficient, as measured on one sample with H/V = 0.73 (Figs. 3 and 4) near the phase transition at $T_c = 201.5$ K. As seen from the figure, relation (2) is satisfied in this case in the temperature interval $(T_c - T) < 22.5°$. The deviation from a straight line at small values of $(T_c - T)$, just as in the case of the phase transitions mentioned above[30,33,35-37] can be due to the fact that the measured dependences near T_c are distorted by inhomogeneities (domains, structural imperfections), by the contribution of linear and relaxation effects, and by inexact satisfaction of the isothermy condition in the dynamic measurements. The fact that the obtained experimental dependences of G and α satisfy relation (2) indicates, first, that this transition is of second order and second, that the measured anomalies at $(T_c - T) < 22.5°$ are not noticeably distorted as a result of the influence of the indicated factors.

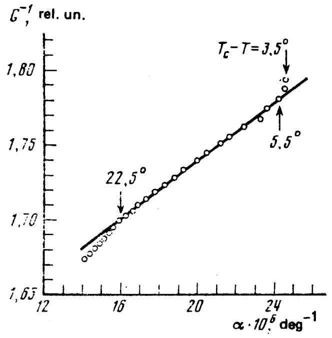

FIG. 6. Dependence of the reciprocal of the elastic modulus on the coefficient of linear expansion along the λ line for the phase transition at $T_c = 201.5$ K in $VH_{0.73}$.

3. *Comparison with the deductions of the theory*. By now, enough experience has been gained in the investigation of phase transitions in solids by measuring the anomalies of the velocity and damping of sound near T_c.[13,14] The character of these anomalies makes it possible to identify the order of the transition, as well as to investigate its dynamic and static characteristics.

Acoustic effects connected with phase transitions can be divided into dynamic, which include relaxation and fluctuation mechanisms (which determine the anomalies of the damping and velocity of the sound), and static (which determine the anomaly of the speed of sound). The most completely investigated relaxation mechanisms[13,14] lead to λ-shaped damping anomalies, inasmuch as the order-parameter relaxation time determined by the equation $d\eta/dt = -L(dF/d\eta)$ (Ref. 14) increases without limit as $T \to T_c$, since the term $dF/d\eta$ tends to zero (here L is a constant coefficient and F is the free-energy density).

The static effects that determine the change of the speed of sound near T_c can be obtained from the term $F(\eta, \varepsilon)$ in the (Landau) expansion of the free-energy density, which describes the interaction between the strain ε and the order parameter η. By examining the leading terms of lowest order in the expansion of F one can find for a continuous phase transition[13] that the dependence of the elastic constants on the temperature is of the type $\Delta G \propto (T - T_c)^{-1}$ in the case of linearity in the order parameter and in the strain, $F \propto \eta\varepsilon$, that $\Delta G \propto (\partial^2 F/\partial\eta^2)\langle\eta\rangle^2$ in the case of a quadratic dependence on the order parameter, $F \propto \eta^2\varepsilon$, and that $\Delta G \propto \langle\eta\rangle$ in the case of a quadratic dependence on the order parameter, $F \propto \varepsilon\eta^2$. The first two cases correspond to V-shaped and jumplike anomalies of the elastic modulus. In the last case, when the largest (predominant) term in the expansion of $F(\eta, \varepsilon)$ is $\eta\varepsilon^2$, the change of the elastic modulus is proportional to the static value of the order parameter, $\Delta G \propto \eta$. Judging from the character of the anomalies of the speed of sound, the phase transition in niobium and vanadium hydrides, considered above, can be attributed just to the latter case.

As noted, however, in Sec. 4.2, the equivalence of the elastic modulus to the static value of the order parameter, which follows from thermodynamic considerations, may be violated for a number of reasons. First, the temperature dependences of the elastic modulus may contain a contribution from the moving domain walls (if the latter exist). Second, as noted in Sec. 3.1, the high-temperature phase transitions in hydrides are sometimes hindered. Third, since the relaxation time of the order parameter becomes very large as $T \to T_c$, the measured $G(T)$ dependence may deviate from the equilibrium dependence if the adiabaticity conditions are not maintained (very low heating rates or prolonged soaking at temperatures near T_c, as e.g., in Ref. 38).

The absence of a noticeable influence of the first two factors was experimentally verified (to be sure, for different transitions) by the satisfaction of the Pippard relation for the $G(T)$ and $\alpha(T)$ dependences (see Sec. 4.2), by the absence of a dependence of the elastic modulus in the case of prolonged soaking of the sample below the transition temperature, and by the independence of the plots of the modulus of the rate of sample heating (see Sec. 3.1). The last circumstance shows, in addition, that experiments, at least in the temperature region where the exponent β is defined (see the table), correspond to adiabaticity conditions. A comparison of the results listed in Table I with the known published data (Tables VI and XIV in Ref. 39) shows that the lower limit of ε for all the considered transitions greatly exceeds the lower limit of ε reached in the case of phase transitions in magnets or gases. [The causes of the deviation of the plots of the elastic modulus from the $(-\varepsilon)^\beta$ law at small ε were considered in Secs. 3.1 and 4.2.] It is precisely because the adiabaticity condition is easier to satisfy at relatively large ε that sample heating rates 0.05–0.2 deg/min turn out to be low enough to obtain equilibrium curves.

4. *Critical behavior*. The arguments advanced in the preceding section allow us to conclude that the measured $G(T)$ dependences near the phase-transition points are compatible with a static the order parameter $\langle\eta\rangle$. In this case a power-law approximation of $G(T)$ near T_c yields a critical exponent β defined by the relation

$$\langle\eta\rangle \propto (-\varepsilon)^\beta. \tag{3}$$

As seen from Table I, the critical exponents β for all the considered transitions are close to 1/3. This shows that for all three phase transitions near T_c there exist regions where the order parameter fluctuates. This result seemed at first to contradict the ideas concerning the character of the phase transitions of hydrogen in metals. Indeed, hydrogen entering the interstices displaces the ions of the metal matrix, as a result of which long-range interaction sets in via the elastic-stress fields.[40,41] Since it is known that long-range action suppresses the critical fluctuations, it was assumed that the phase transitions in hydrides should agree exactly with the Landau theory (the mean-field approximation). These opinions were confirmed experimentally in a study of the critical state in the systems Pd-H and Nb-H. It was noted that there is no maximum of the heat capacity[42] and no critical scattering of neutrons[43] near the critical point in these hydrides. The critical exponents obtained for both systems correspond to the "classical" values ($\beta = 1/2$, $\delta = 3$).[44] In contradiction to these results, only in Ref. 45 were values $\beta = 0.33$ and $\delta = 4.2$ obtained for the critical point of the hydride of $\mathrm{PdAg}_{0.1}$.

Recently, however,[46] using x-ray diffractometry, a phase separation line was quite accurately constructed for the Nb-H system near the critical point (H/Nb = 0.31, $T_c = 444$ K), and the critical exponent was found to be $\beta = 0.37^{+0.03}_{-0.02}$. The authors of Ref. 46 believe that the difference between their results and those previously obtained by others is due to the fact that the samples usually employed for the measurements are cooled after the introduction of the hydrogen (at $T \sim 900$ K) to room temperature (i.e., below the phase-decay temperature). Inasmuch as in Ref. 46 the measurements were made immediately after saturation of the samples with hydrogen, while installed in the apparatus, the appearance of non-coherent inclusions of the α' phase, which damage irreversibly the crystal structure of the metal (dislocations, internal stresses) was excluded. This assumption is confirmed by the results of calorimetric measurements, in which it was shown that the internal stresses lead to a strong broadening of the maximum of the heat capacity near T_c in niobium hydride.[47]

Thus, according to the results of Ref. 46, the critical behavior of metal-hydrogen systems depends substantially on the perfection of the samples. It should be noted that the hydrides used in these investigations satisfy these requirements. Even though the samples were saturated with hydrogen not in the measurement setup, as in Ref. 46, the perfection of the initial structure of the metals was not violated because of the use of a saturation regime wherein there was no crossing of the line separating phases with large specific-volume difference.

The experiments, in which a critical behavior was observed for the first time ever in ordered metallic systems, have yielded quantitative results only for the static critical exponent β and for the width of the critical region. It is undoubtedly of interest to determine the other characteristics of these phase transitions. This calls primarily for dynamic measurements (acoustic methods, neutron scattering), as well as for information on the structure of the low-temperature phases.

5. CONCLUDING REMARKS

What makes metal-hydrogen systems attractive is primarily that they combine a crystal structure with kinetic properties (of the hydrogen sublattice) similar to those of normal liquids. It was noted in Ref. 1 that metal hydrides serve as a convenient model for research into the physics of phase transitions. Indeed, the study of the decay of a solid solution of hydrogen in palladium, niobium, and tantalum has yielded many important results.[48]

The investigations of the static characteristics of low-temperature phase transitions in niobium and vanadium hydrides have shown that metal-hydrogen systems can be no less convenient a model also for the investigation of phase transitions of the ordering type. The main experimental difficulties in the study of the ordering of binary metallic systems (CuAu, Cu$_3$Au,...) are connected with the long time required to establish the equilibrium order parameter, which reaches in certain cases tens of hours.[19,49] For measurements of the anomalies of the physical quantities near T_c with sufficient accuracy, it would be necessary to perform experiments lasting several months. In the case of a metal-hydrogen system, as is seen from the results of the present paper, quasicontinuous curves are obtained after 20–40 hours, i.e., approximately 100 times faster. This circumstance will apparently make it possible to perform on such model systems experiments of a new type, heretofore unconceivable if only because of the necessary time scale.

The results of the present paper show that the mobility of hydrogen at temperatures ~100 K is so large, that in the investigation of hydrides near phase transitions of the ordering type one observes fluctuations of the order parameter. Such a phenomenon is apparently impossible in other ordered solid systems (with the possible exception of superionic crystals), because of the hindered diffusion kinetics.

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