STUDY OF THE ORDERING OF INTERSTITIAL ATOMS IN SOLID SOLUTIONS OF HYDROGEN IN GROUP V METALS

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STUDY OF THE ORDERING OF INTERSTITIAL ATOMS IN SOLID SOLUTIONS OF HYDROGEN IN GROUP V METALS

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1. Recently, interest has increased in the problem of order–disorder phase transitions ($^{1-4}$) in interstitial systems. The possibility of the existence of such transitions follows directly from the fact that, ordinarily, in interstitial solid solutions the number of interstices exceeds the number of interstitial atoms. It is natural to expect that at high temperatures a statistical distribution of interstitial atoms over interstices is realized, whereas upon lowering the temperature a "crystallization" of interstitial atoms in the crystal field of the matrix atoms is possible. Important information on transitions of this type can be obtained by studying neutron scattering. This is due to the fact that, in most cases, interstitial solid solutions are systems consisting of atoms that differ greatly in mass, and localization of the lighter atoms by means of X-ray structural analysis is difficult because of their weak scattering power. At the same time, neutron-diffraction methods are free from these shortcomings.

A typical example of interstitial systems is provided by solid solutions of hydrogen in metals. It is known that hydrogen dissolves well in the Group V metals V, Nb, Ta, forming interstitial solid solutions over a wide concentration range. The Me—H phase diagrams, identical for all three systems, show that upon lowering the temperature the solid solutions of hydrogen in the metal decompose with the formation of two phases (α and β). According to X-ray studies ($^{5-8}$), the metal atoms in both phases form a body-centered cubic structure, slightly distorted in the β-phase. The positions of the light atoms could not be determined by the X-ray method.

Table 1

Sample	Thermal effects, °C	Thermal effects, °C
	not accompanied by gas evolution	associated with decomposition of samples
$NbH_{0.80}$	78—87	380—410; 480—510

Fig. 1. Neutronogram of ordered niobium deuteride. $NbD_{0.95}$; $T = 20^\circ$

Figure 1: Fig. 1. Neutronogram of ordered niobium deuteride. $NbD_{0.95}$; $T = 20^\circ$

Fig. 2. Structure of ordered niobium deuteride

Figure 2: Fig. 2. Structure of ordered niobium deuteride

Sample	Thermal effects, °C	Thermal effects, °C
$NbH_{0.95}$	140–160	380–415; 475–510
$NbD_{0.93}$	160–180	385–415; 475–510
$TaH_{0.81}$	80–92	460–525
$TaD_{0.81}$	105–115	480–555
$VH_{0.80}$	(−90)–(−70°)	415–425
$VD_{0.80}$	–	420–430

2. In connection with this, in the present work hydrides and deuterides of V, Nb, and Ta with compositions close to MeX were investigated by elastic neutron scattering. The purpose of the measurements was to establish the arrangement of the light atoms and the nature of possible phase transformations in these hydrides. Data from thermographic analysis were used to determine the temperatures of the phase transitions.

Samples of the hydrides and deuterides of the compositions indicated in Table 1 were prepared in the laboratory of hydride chemistry of the Institute of General and Inorganic

of Chemistry named after N. S. Kurnakov on an apparatus fundamentally no different from that described earlier ([9]). The neutronographic investigations were carried out on a vertical neutron diffractometer ([10]) installed at the heavy-water research reactor of the I. V. Kurchatov Institute of Atomic Energy. To obtain a monochromatic neutron beam, a bent crystalline monochromator of silicon iron was used ([11]). Recording of the differential and simple heating curves was carried out on a Kurnakov pyrometer and was accompanied simultaneously by registration of the volume of gas evolved.

3. In neutronograms of Nb and Ta deuterides and hydrides obtained at room temperature, in addition to peaks characteristic of the body-centered structure of the metal, additional superstructure reflections were detected (Fig. 1). Similar superstructure reflections occur in the neutronogram of vanadium deuteride obtained at liquid-nitrogen temperature. Since the symmetry of the interstitial sites coincides with the symmetry of the b.c.c. lattice of the metal, a statistical arrangement of interstitial atoms

Fig. 1. Neutronogram of ordered niobium deuteride. $NbD_{0.95}$; $T = 20^\circ$.

Fig. 3

Figure 3: Fig. 3

Fig. 2. Structure of ordered niobium deuteride.

cannot give superstructure reflections; consequently, the presence of superstructure reflections in the neutronograms shows that at low temperatures hydrogen and deuterium atoms occupy a portion of voids of a definite type. As a result of indexing the neutronograms, it was established that the light atoms are arranged in an ordered manner in tetrahedral interstices. The structure of the ordered phase (Fig. 2) (space group $D_{2h}^2/Pnnn$, Me in f, D in a and b) is characterized by the fact that the hydrogen atoms are located at distances differing little from one another in comparison with other possible arrangements, i.e., in the most uniform manner. This fact apparently indicates that the light atoms are ionized. With increasing temperature the intensity of the superstructure peaks decreases, which indicates disordering-

diffusion of interstitial atoms (“melting” of the sublattice) (Fig. 3). To explain the structure of the high-temperature phase, two alternative models may be proposed, giving equally satisfactory agreement with the experimental values of the intensities (Fig. 4). A number of data, however, testify in favor of the model according to which the transition from the completely ordered state to the completely disordered state occurs in a stepwise manner.

4. The order-disorder transition temperatures determined neutronographically agree with the data of thermographic analysis. The thermograms obtained, superposed on the gas-evolution curves, reveal, in addition to effects associated with thermal dissociation, reversible endothermic effects at a lower temperature. The values of the temperatures of the phase transitions increase from VD to TaD, and also with increasing concentration of light atoms. It has also been established that replacement of hydrogen by deuterium leads to an increase in the transformation temperatures by approximately 20°, without having a substantial effect on the decomposition temperature of the samples.

Fig. 3. Neutronogram of niobium deuteride above the order-disorder transition point. NbD; $T = 210^\circ$

5. Using the group-theoretical method developed by A. G. Khachaturyan (^{12}), the problem of ordering of impurity atoms over the tetrahedral interstices in a b.c.c. cell was considered. For the composition MeX a solution was obtained that fully corresponds to the structure proposed in the present work for the hydrides and deuterides of Group V metals. It is characteristic that formation of this structure can occur stepwise. A number of other superstructures corresponding to the compositions MeX_2, MeX_3, etc., were also obtained. Some of these superstructures have been observed experimentally.

Fig. 4

Figure 4: Fig. 4

Fig. 4. Models of disordering in hydrides and deuterides of Group V metals

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