ON THE STRATIFICATION OF THE SYSTEMS H_2--HD AND D_2—HD IN THE SOLID PHASE

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X-ray structural analysis methods were used to determine the mutual solubility of D_2 and HD molecules and of H_2 and HD molecules, at 4.2°K. It is shown that the solubility in these two systems, as in the D_2—H_2 system,[5] is limited. The region of statification found in the systems D_2—HD and H_2—HD is not symmetric with respect to the concentration and is shifted toward the heavier isotope.

BEGINNING in 1954, Prigogine,[1] I. M. Lifshitz and G. I. Stepanova [2] published a series of communications in which they presented a theory of isotopic solutions. The most important achievement of this theory is the prediction of phase stratification at sufficiently low temperatures. This phenomenon has been observed experimentally in the liquid [3] and solid [4] He^3—He^4 systems, in solid systems consisting of hydrogen isotopes,[5-7] and in the liquid systems Ne—nD_2 [8] and Ne—pH_2.[9]

In the present, work the x-ray diffraction method was used to determine approximately the solid-state solubility limits of the systems D_2—HD and H_2—HD at 2.4°K. The system H_2—D_2 has, as reported earlier,[5] a stratification region in the solid phase. This has been deduced from x-ray diffraction patterns for a wide range of concentrations of H_2—D_2 solid solutions, which show clearly two systems of diffraction lines of the solid solutions of limiting concentrations. Samples of H_2—HD and D_2—HD isotopic mixtures were prepared by condensing them from the gaseous phase on to a copper substrate cooled from inside with liquid helium. Since, under our conditions (the Debye diffraction pattern of a condensate deposited on the side surface of a cylindrical copper capillary cooled from inside with liquid helium) the diffraction patterns of solid H_2, D_2, and HD had very few rings, which were concentrated in a narrow range of angles and could overlap, we could establish the presence of stratification only from the intensity, width and profile of the diffraction lines. Figure 1 shows photometric curves of the line intensity for x-ray diffraction patterns of samples of various concentrations, recorded at 4.2°K. It is evident from this figure that the lines of pure D_2 and HD have sharp minima, while the lines of deuterium-rich mixtures are broad, their width being about twice
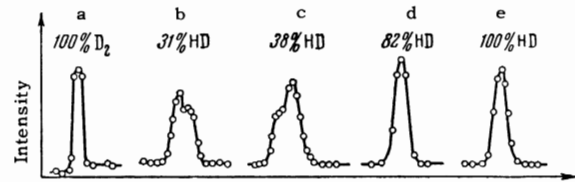

FIG. 1. Microphotograms of the diffraction lines of the D_2—HD mixtures of various compositions.

the line width for pure components. The doublet nature of these lines is clearly visible, indicating the simultaneous presence of two phases with slightly different lattice parameters.

The dependence of the unit cell volume on the concentration was determined for the system D_2—HD. This dependence is shown in Fig. 2, from which it is evident that: 1) there is a region of concentrations in which the solid solution splits into two phases which have different deuterium and deuterium hydride contents (the stratification region is asymmetric and shifted toward the heavier isotope); 2) in the concentration region $\approx$50—100% HD, i.e., in the solid-solution region, there is a departure from the additivity.

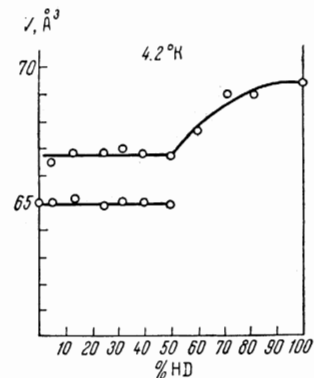Similar investigations were carried out on

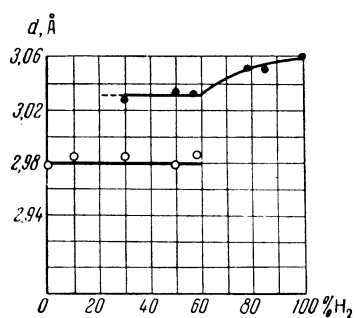FIG. 2. Dependence of the unit cell volume of the solid solutions D_2—HD on the composition.

FIG. 3. Dependence of the interplanar distance in the lattices of the solid solutions H_2–HD on the composition.

H_2—HD mixtures. The results are given in Fig. 3, which illustrates the dependence of the interplanar distance on the composition.

In the concentration region from approximately 10 to 60% H_2, there are two systems of interplanar distances, which correspond to phase stratification.

In the concentration region from ≈60 to 100% H_2, there is a positive departure from the ideal system, as in the D_2—HD system.

If we draw the approximate contours of the stratification curves, with allowance for the determined solubility limits and for the critical temperatures deduced from the formulas given by Lifshitz and Stepanova,[2] we can see (Fig. 4) that the regions of phase stratification in the hydrogen isotope solid solutions are asymmetrical and the maxima of the stratification curves lie in the region of 30% of the lighter isotope.

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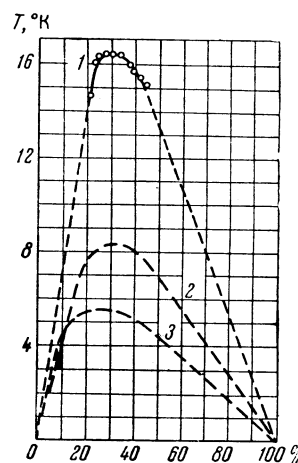

FIG. 4. Stratification curves for the systems: 1) H_2–D_2; 2) H_2–HD; 3) HD–D_2. The abscissa gives the concentration of the lighter isotope.

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