

FIG. 1. Superconducting transition temperature of some B-B phases obtained under pressure.^{2,3}

tures with a lower packing density (coordination number): fcc, hcp $(12) \rightarrow bcc (8) \rightarrow simple hexagonal (2 + 6)$

 $\rightarrow\beta$ -Sn(4+2) \rightarrow simple cubic (6).

For metallic phases with $n_e > 3$ electrons/atom the characteristic structures are simple hexagonal (γ) and simple cubic (π), and also their distorted variants. These phases are a continuation of a series of well-known electronic Hume-Rothery phases, characteristic for alloys of B elements with $n_e = 1-2$ electrons/atom.

The range of B-B phases, substantially extended over the last decade, makes it possible to study correlations between the superconducting properties (T_c), structure, and electron density of alloys (see Fig. 1).

1. Within the limits of stability of each structural type T_c increase monotonically as n_e increases. It is interesting to note that in following each curve, in accordance with the data from x-ray structural analysis, the electron density n_e/v electrons/Å³ remains approximately constant.

2. For the same values of n_e in different alloys of elements of V and VI periods, close values of T_c were obtained for phases with the same structure.

3. Comparison of data on T_c for alloys with the same electron density but different structure shows that higher values of T_c are characteristic for the more compact structures.

4. For phases with the same type of structure, higher values of T_c are achieved in alloys with lighter components. For fcc solid solutions of silicon in alumina a value of $T_c = 11$ K, the highest value for alloys of transition elements, was obtained.³

The new class of superconducting B metals studied, in view of the simplicity of their electronic structure, high symmetry of their crystalline structure, and also the simple and unique correlations between T_c , the electron density, and the structure, is a convenient model system for further development of the theory of superconductivity. We note that this class of superconductors was ignored in previously published reviews on superconductivity, including the last two reviews in Uspekhi Fizicheskikh Nauk.⁴

In conclusion, we would like to call attention to an interesting effect of the pressure on the structural state of alloys, though not predicted beforehand, but still entirely natural and explainable—the process whereby alloys are rendered amorphous. The amorphous state appears in alloys with "quenched" high-pressure phases as an intermediate metastable step along the path back to the equilibrium state. As a rule, we observe the amorphous state in alloys which have in the equilibrium state a semiconducting phase (in the alloys Zn–Sb, Cd–Sb, and Al–Ge, these are ZnSb, CdSb, and Ge, respectively).

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V. V. Brazhkin, V. I. Larchev, S. V. Popova, and G. G. Skrotskaya. Metallic glasses and amorphous semiconductors, obtained by quenching from the melt under high pressure. Interest in the study of amorphous materials under high pressure has led to extensive investigations of their properties (electrical conductivity, superconductivity, phase transitions, etc.) with the help of the entire arsenal of experimental methods developed previously for crystalline materials. In addition, it has been shown in recent years that pressure can also be used as a method for obtaining amorphous materials. One of these methods is the method of quenching from the melt under a constant pressure up to 10 GPa with a cooling rate of 10^2-10^4 K/s.

Analysis of the processes of nucleation and growth of

crystals in a supercooled melt indicate that pressure has a substantial effect on both processes. Quantitative estimates can be made in the approximation of homogeneous nucleation for elementary metals and superconductors using existing data on the thermodynamic quantities characterizing melting and their derivatives with respect to pressure as well as model representations of the pressure dependences for activation energies of nucleation and growth of crystals. For substances for which the jump in the volume on melting is positive, the rate of homogeneous nucleation under low pressures (up to 50 kbar) can both increase and decrease by one to two orders of magnitude (by a factor of $10-10^2$). Under quite high pressures (100-150 kbar) the rate of nucleation should decrease by three to five orders of magnitude. The

rate of growth of the crystals decreases in the entire pressure range and at P = 50 kbar this decrease constitutes one to four orders of magnitude from the rate of growth under atmospheric pressure. The maxima of the functions of the rate of nucleation and growth of crystals are displaced into the region of lower supercoolings. As a result, the critical rate of cooling, required for obtaining an amorphous state under a pressure of up to 50 kbar, can both decrease and increase, and under high pressures of \sim 150 kbar it must decrease by three to seven orders of magnitude. For substances with a negative jump in the volume upon melting the rate of nucleation and rate of growth apparently decrease with the pressure, and in addition the scale of the change in the rate of growth is smaller than in the first case. A systematic analysis of the effect of pressure on the nucleation and growth of crystals becomes much more complicated if the possibility of phase transitions in the solid or liquid state is taken into account.

The effect of pressure on rapid quenching of copper-tin alloys was studied experimentally. It was shown that in a definite region of compositions (12-17 at. % tin) x-ray amorphous alloys are formed.¹ The short-range ordering of such alloys can be described equally based on both the microcrystalline model of hexagonal close packing and the chaotic close packing of solid spheres. Under atmospheric pressure metallic glasses in this system can be obtained from the melt with cooling rates of 10^{10} K/s,² while under a pressure of 50 GPa the corresponding cooling rates are only $2 \cdot 10^3$ K/s.

Figure 1 shows the radial distribution function of the atoms of the alloy $Cu_{0.85} Sn_{0.15}$, obtained by quenching from the melt under pressure. The figure also shows for comparison the radial distribution functions, taken from Ref. 3, of



FIG. 1. Atomic radial distribution functions of copper-tin amorphous alloys obtained by sputtering (broken lines) (data of Ref. 3) and of the alloy $Cu_{0.85}$ Sn_{0.15} (solid line) obtained by quenching from the melt under a pressure of 5 GPa.



FIG. 2. Change in the diffraction pattern accompanying an increase in the content of the amorphous phase x in gallium antimonide, obtained by quenching from the melt under a pressure of 9 GPa. x = 0 (a), 0.36 (b), 0.7 (c), and 1.0 (d).

sputtered amorphous films with different compositions.

High pressure enabled obtaining for the first time by means of quenching from the melt bulk amorphous samples of $A^{III}B^{V}$ compounds (gallium antimonide),⁴ which under ordinary conditions appear only in the form of thin sputtered films. X-ray structural and optical (Raman light-scattering spectra) investigations of amorphous gallium antimonide show that the structure of the quenched samples is similar to that of thin amorphous films. This result suggests that the formation of amorphous tetrahedral phases under pressure occurs by means of quenching of metallic glass when the melt is coded under isobaric conditions followed by a transition of the metallic glass into the amorphous semiconducting phase as the pressure is lowered.

Under atmospheric pressure amorphous gallium antimonide crystallizes at 445 K with a liberation of heat equal to $8/7 \pm 1.4$ kJ/mole.⁵ By varying the conditions of quenching from the melt it is possible to obtain a sample with different content of the amorphous phase $0 \le x \le 1$. The value of the parameter x can be determined quantitatively from the relative values of the heats of crystallization. Figure 2 shows the change in the diffraction pattern of the samples with different content of the amorphous phase.

As the content of the amorphous phase in the system $(\text{amorphous GaSb})_x$ (crystalline GaSb)_{1-x} increases, a metal-insulator transition, caused by the disordering of the crystalline structure (the content of the amorphous phase x plays the role of the order parameter), which can be described on the basis of the scaling theory, occurs.⁶

The theoretical and experimental results obtained show that pressure has a substantial effect on the kinetics and thermodynamics of solidification of supercooled melts and they demonstrate that this method could be useful for preparing metallic glasses and amorphous semiconductors.

¹V. V. Brazhkin and S. V. Popova, Metallofizika 7, 103 (1985).

V. E. Antonov, I. T. Belash, and E. G. Ponyatovskii. Hydrides: investigations under high hydrogen pressures. The study of high-pressure phases in metal-hydrogen systems began at the Institute of Solid State Physics of the USSR Academy of Sciences in the mid-1970s after the invention of a quite simple and effective method for compressing gaseous hydrogen to high pressures.¹ Application of the method¹ made it possible to achieve record high hydrogen pressures up to 90 kbar (the highest pressure achieved abroad equals 30 kbar), which, in particular, made it possible to obtain and study hydrides of all 3d metals and all 4d metals with the exception of ruthenium, as well as hydrides of different alloys based on these metals.

Metals of the 3d series and their alloys exhibit magnetic order, and the possibility of saturating these metals with hydrogen up to high concentrations has in its turn opened up the possibility of studying the effect of hydrogen on the magnetic ordering in d metals. At first we had to endure a quite prolonged stage of accumulation of primary experimental information on the composition, crystalline structure, and magnetic properties of hydrides, forming under high hydrogen pressures, based on different 3d metals and their alloys. After this stage was completed two important facts became clear. First, hydrides are formed on the basis of only the two simplest packings of the atoms of the metals-fcc or hcp. Second, the effect of hydrogen on the magnetic properties of a magnetic material can be very diverse depending on the type of magnetic material being hydrated. For example, antiferro- and paramagnetic materials can transform into ferromagnetic materials, the spontaneous magnetization of the ferromagnetic materials can increase, the Curie points can decrease, and vice versa both these quantities can decrease, increase, or change nonmonotonically, etc.

But, probably the most interesting fact is that all diverse effects can be systematically explained and described under one assumption: the magnetic properties of the metals and alloys studied change under hydrogenation as a result of the increase in the degree of filling of their d bands with electrons, and in addition the hydrogen must be regarded as the donor of a fractional number of electrons $\eta < 1$ electrons/H atom. We note that the idea of hydrogen as a donor of a fractional number of electrons to the d band of the metal-solvent agrees with the results of calculations of the band structures of nickel and palladium hydrides, carried out by other authors.

Study of the influence of hydrogen has also made it possible to clarify the factors responsible for some of the features on the concentration dependences of the magnetic properties of alloys of 3d metals without hydrogen, and the follow⁵M. M. Aleksandrova, V. D. Blank, V. I. Larchev, S. V. Popova, and G. G. Skrotskaya, Phys. Status Solidi B **91**, K5 (1985).

⁶M. M. Aleksandrova, S. V. Demishev, Yu. V. Kosichkin, V. I. Larchev, S. V. Popova, and G. G. Skrotskaya, Pis'ma Zh. Eksp. Teor. Fiz. **43**, 182 (1986) [JETP Lett. **43**, 230 (1986)].

ing situation has now been achieved: if the composition of the alloy (let it be multicomponent) based on iron, cobalt, or nickel is given, then it is possible to predict *a priori* its magnetic properties in the fcc or hcp modifications, and also the effect of the interstitial hydrogen on these properties.²

As regards the properties of the hydrides of 4d metals and their alloys, here the study of superconductivity is of greatest interest. We began with the study of hydrides of alloys of palladium with Cu, Ag, and Au, since previously, by means of implantation of hydrogen into these nonsuperconducting alloys, samples with a superconducting transition temperature T_c up to ≈ 17 K were obtained (see Ref. 3), while theoretical estimates of the values of T_c for Pd-Ag-H hydrides gave values of up to ≈ 50 K.⁴ Our measurements on massive homogenous samples of hydrides obtained under high pressures, however, showed that these effects are not observed in Pd-noble metal-H systems, and, therefore, high values of T_c for hydrides with implanted hydrogen were determined specifically by the characteristics of the samples obtained precisely by this method.

This result made it necessary to analyze critically the existing information on the superconductivity of hydrides of d metals, and it turned out that the situation is not much different from the situation which existed at the starting stage of the study of magnetic properties of hydrides of 3d metals: correct data for massive single-phase samples are in fact limited by the fact that the superconducting properties of Pd hyrides have been studied in great detail, while super-conductivity has not been observed in the hydrides of Ti, Zr, Hf, V, Nb, and Ta, and that there is no theory or even empirical recipes for further searching for superconducting hydrides.

To evaluate the role that a change in the degree of filling of the conduction band of the metal-solvent by electrons can play in the change in T_c accompanying hydrogenation we studied the influence of hydrogen on T_c of the bcc alloys Nb-Ti, which are convenient for this purpose, and for all alloys studied we observed a sharp (≈ 15 K/H atom) drop in T_c . This effect cannot be explained by a change in the electron density of the alloys and must necessarily be attributed to the change in their phonon spectrum. This implies that in the case of hydrogen solutions one can hardly depend on the predictions of the rigid-band model, satisfactorily describing the concentration dependences of T_c for alloys of dmetals without hydrogen, and in order to search deliberately for new superconducting hydrides other guideposts must be sought.

For such a quidepost we employed the published data on the fact that hydrogen-saturation of niobium alloys with

²I. S. Miroshnichenko Quenching from the Liquid State (in Russian), Nauka, Moscow (1982), p. 168.

³H. Zeitz, Z. Phys. K1, B 40, 65 (1980).