

E. G. Ponyatovskii. *High-pressure phases in condensed systems and metal-gas systems*. In his program papers,<sup>1</sup> "Which problems in physics and astrophysics are especially important and interesting at this point?," V. L. Ginzburg added to a list of ten such problems that of phase transitions and critical phenomena and that of producing new materials with unusual properties. A constant stimulus to the development of research in these interesting directions in modern solid-state physics is the experimental progress being obtained at high pressures. This report summarizes some results on isomorphic transitions in solids and high-pressure phases in metal-hydrogen systems from work carried out in the Laboratory of High-Pressure Physics at the Institute of Solid State Physics of the Academy of Sciences of the USSR.

An experimental study of the effect of pressure on an isomorphic conversion in cerium in 1958 (Ref. 2) led to the conclusion that the curve representing this conversion should terminate at a liquid-vapor critical point. It should be noted that the suggestion that critical points of this type could occur on phase-transition lines in solids contradicted the ideas prevalent at the time.<sup>3</sup> Subsequent experiments confirmed the conclusion of Ref. 2, however, and it has now received a theoretical basis.

Research on isomorphic conversions in solids has been one of the primary fields of activity of the Laboratory since its organization. A long list of materials has been found in which the isomorphic transition terminates in a critical point. Particularly interesting are the phase diagrams of the compound SmS and its alloys, which exhibit such a highly unusual phenomenon<sup>4</sup> as the presence of critical points at both ends (the high- and low-temperature ends) of an isomorphic-conversion line (Fig. 1). Experiments on the effect of the doping of SmS by other rare earths indicate that it is possible to bring the critical point up to atmospheric pressure and to room temperature; this possibility opens up some tempting new possibilities for direct experimental study of critical anomalies in solids and for the practical use of these anomalies.

The experimental work has been accompanied by the development of thermodynamic models for isomorphic transitions in the materials which have been studied. A phenomenological approach which has been developed in the Laboratory is based on the representation of these materials as pseudosolutions of ions in various

valence states. This approach has furnished a quantitatively correct description of the data available on the corresponding phase diagrams and on the pressure and temperature dependences of the volume properties. This approach has also generated predictions of several aspects of the behavior of these properties near the critical points. The models which have been developed contain a minimum number of adjustable parameters. The properties of cerium, for example, can be described well by a model of pseudobinary solutions which uses only experimental data on the specific volumes of both isomorphic phases at atmospheric pressure and on the coordinates of the critical point.<sup>5</sup> A model of pseudoternary solutions has recently been developed for SmS and its alloys. This model puts ions with an intermediate valence on an equal footing with ions with an integer valence. This model gives a good description of both the rather complicated phase diagrams (Fig. 2) and the physical properties of SmS-GdS solid solutions.

The appeal to representations regarding pseudosolutions with effective concentrations as internal parameters has made it possible to develop a unified description of some conversions markedly different in nature. For example, the same formalism has successfully described the characteristics of the stimulated UV radiation from the isostructural transition in crystals with the dianthracene structure; this transition also terminates in a critical point.<sup>6</sup>

Another promising direction in the recent research in the Laboratory is the study of high-pressure phases in metal-hydrogen systems. In the mid-1970s, a method

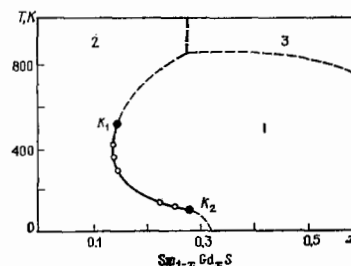


FIG. 1.  $T, x$  Diagram of the system  $\text{Sm}_{1-x}\text{Gd}_x\text{S}$  in the region of isostructural isoconcentration transitions. 2, 3, I—Regions in which  $\text{Sm}^{2+}$ ,  $\text{Sm}^{3+}$ , and  $\text{SmI}$  ions, respectively, are predominant ( $\text{SmI}$  are intermediate-valence ions);  $K_1, K_2$ —critical points; solid curve—first-order transitions; dashed curves—supercritical anomalies.

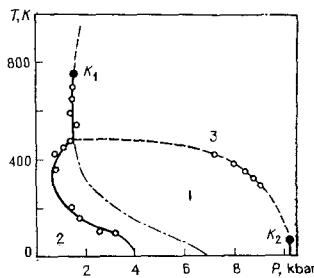


FIG. 2.  $T, P$  Diagram of the alloy  $\text{Sm}_{0.87}\text{Gd}_{0.13}\text{S}$ . The notation is the same as in Fig. 1.

was developed in the Laboratory for compressing hydrogen to tens of kilobars in volumes permitting the hydrogenation of relatively massive samples, including metals previously considered immune to hydrogenation.<sup>7</sup> Compressing hydrogen to 20 kbar has made it possible to produce the hydrides  $\text{MnH}_{0.96}$ ,  $\text{NiH}_{1.25}$ , and  $\text{TcH}_{0.8}$  (these are the maximum compositions); compressing it to 65 kbar has made it possible to produce the hydrides  $\text{FeH}_{0.8}$ ,  $\text{CoH}_{0.5}$ ,  $\text{MoH}$ , and  $\text{RhH}_{0.65}$ . A year ago, hydrogen was compressed to 90 kbar; this achievement made it possible to saturate rhenium to the composition  $\text{ReH}_{0.22}$  and to increase the solubility of hydrogen in cobalt to  $\text{CoH}_{1.0}$ . In addition, scandium trihydride and gold hydride have been produced; the latter is the first hydride of a noble metal.

In terms of the physical properties, the most interesting results include those obtained in research on the magnetic properties of solid solutions of hydrogen in 3d metals and their alloys (in Ni, Co, Fe, and Mn and in the alloys Ni-Cu, Ni-Co, Ni-Fe, Ni-Mn, Ni-Cr, Fe-Mn, and Fe-Ni-Mn; the examples we have cited here have been chosen to illustrate as many of the known types of band magnetic materials as possible).<sup>8</sup> Analysis of all the data available has led to the conclusion that the primary effect in the magnetic properties of group VI-VIII transition metals upon hydrogenation is an increase in the extent to which their d bands are filled with electrons. The hydrogen furnishes a fractional number of electrons,  $\eta < 1$  electron/proton, to the d band of the solvent metal. Study of the magnetic properties has thus made it possible to determine the physical status of hydrogen (in particular, its charge state) in group VII and VIII transition metals. A model of a rigid d band has been proposed to describe the concentration dependence of the magnetic properties of Me-H solutions. This model furnishes a noncontradictory explanation of all the experimental data available, and it predicts the behavior of these properties in some cases which have not yet been studied. It should be noted that the representation of hydrogen as the donor of a fractional number of electrons to the d band of a solvent metal agrees with results calculated on the band structures of nickel and palladium hydrides by other investigators.

Some other interesting results have emerged from research on solutions of hydrogen in palladium alloys. Interest in these alloys was first stimulated by published reports of an unusual behavior of the super-

conducting transition temperature  $T_c$  in these solutions resulting from the implantation of hydrogen. The observed effects and the analysis of their possible causes have been the subjects of a fair number of papers (see Ref. 9). Our study of Pd-Cu-H, Pd-Ag-H, Pd-Au-H, Pd-Ni-H, and Pd-Pt-H solutions synthesized at high hydrogen pressures has shown that massive homogeneous samples do not exhibit this anomalous behavior of superconducting properties. The unusual behavior of  $T_c$  of the Pd-Me-H solutions produced by implantation is thus not a property of equilibrium solutions but a consequence of the particular features of the metastable states of the thin, defect-saturated layers of metal into which hydrogen is introduced during the implantation.

Further study has nevertheless shown that Pd-Me-H solutions produced at a high hydrogen pressure do exhibit anomalous properties, but in another area: At relatively low temperatures ( $\geq 250^\circ\text{C}$ ), these solutions exhibit some new phase transitions, accompanied by a diffusive redistribution of the atoms of the metal matrix. In the hydrides of the alloys  $\text{Pd}_{80}\text{Cu}_{20}$  and  $\text{Pd}_{50}\text{Ag}_{50}$ , for example, the metal sublattice undergoes an atomic ordering. The hydrides of the Pd-Ni and Pd-Pt alloys decompose into palladium-rich and palladium-poor phases. These effects indicate that hydrogen has an extremely strong effect on the interatomic interaction and diffusive mobility of the metal components in these hydrogenated alloys. The new phase states of the alloys can be preserved in a metastable state under standard conditions after the hydrogen is removed.

Some other interesting results have been obtained for the hydrides of metals of groups I and III. A study of the phase transitions of solid solutions of hydrogen in the fcc sublattices of the light rare earths has shown that several conversions occur over the concentration interval  $\text{MeH}_2\text{-MeH}_3$ . Phase transitions have been found in the Nd-H system over the entire range of homogeneity of the fcc solutions. Study of the hydrides and deuterides of cerium, which exhibit similar effects, has made it possible to relate these transitions to an ordering of hydrogen in a sublattice of octahedral interstitial positions.

Analysis of the crystal-chemistry relations has generated predictions of structural transitions of the NaCl-CsCl type for the hydrides of K, Pb, and Cs (Ref. 10). A corresponding transition has been observed in KH at a pressure of about 45 kbar. For CsH the transition pressure turned out to be only 7 kbar, and the change in volume at the transition was  $\approx 8.6\%$ , in approximate agreement with the theoretical prediction. A study of quenched phase of high-pressure CsH at atmospheric pressure confirmed that it in fact has a CsCl structure.<sup>11</sup>

We believe that further progress in this research will come from improvements in experimental techniques at static pressures in the megabar range.

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