Anomalies of the superconducting properties of amorphous hydrogenated silicon at high pressures

I. V. Berman, N. B. Brandt, I. L. Romashkina, V. I. Sidorov, and V. A. Alekseev
M. V. Lomonosov State University, Moscow

(Submitted 31 January 1985)
Pis'ma Zh. Eksp. Teor. Fiz. **41**, No. 7, 288–290 (10 April 1985)

At pressures in the range 140–180 kbar, preceding the crystallization of *a*-Si:H, the temperature of the transition to superconductivity, T_c, is significantly (1.5–3 K) higher than in the amorphous and crystalline phases. This increase in T_c may be due to an interaction of electrons with concentration waves in a crystallizing system.

Superconductivity in systems in metastable states has attracted considerable interest. Particularly interesting systems are amorphous substances, in which the application of pressure makes it possible to observe not only the onset of superconductivity near a mobility threshold[1] but also a change in the superconducting properties at pressures near the crystallization pressure.

We have studied the superconducting properties of amorphous *a*-Si:H at high pressures. The amorphous phase of silicon crystallizes at a pressure substantially higher than that at which superconductivity arises.[2] It thus becomes possible to study the changes in T_c as the crystallization pressure is approached and also in the crystalline phases that arise at higher pressures.

The test samples, produced through the decomposition of silane, contain up to 16 at. % hydrogen. The measurements are carried out at pressures up to 220 kbar and at temperatures in the range 1.5–300 K. The pressure is determined within $\pm$ 10% from the shift of T_c of a lead pressure gauge mounted beside the sample. The resistivity is measured by a four-contact method.

Pressure induces an insulator-metal transition (apparently a Mott transition) in the *a*-Si:H system, accompanied by a decrease in the resistance R by seven to ten orders of magnitude. The transition pressure $P_0(X)$ increases with increasing oxygen concentration X from $P_0 = 100$ kbar at $X = 0$ to $P_0 = 170$ kbar at $X = 16$ at. %. At $P > P_0(X)$, but < 140 kbar, the value of T_c in the metallic amorphous phase falls off linearly with increasing P (curve 1 in Fig. 1). At pressures above 180 kbar, according to x-ray diffraction analysis,[2] there is a complete crystallization of the amorphous silicon into a mixture of crystalline phases with bcc and β-Sn structures. The situation in *a*-Si:H is apparently similar.

For the crystallized phases of *a*-Si:H, the P dependence of T_c has a maximum (curve II in Fig. 1). The motion along this curve is completely reversible. The transitions of the crystallized phases to the superconducting state are sharp transitions, although their width increases slightly as the limiting pressure $P \approx 100$ kbar is approached; below this pressure, there is no superconductivity. The disappearance of the

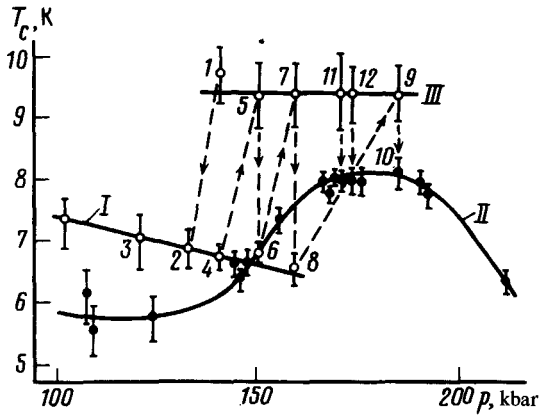

FIG. 1. Pressure-induced changes in T_c of a-Si:H. I—Equilibrium values of T_c of the amorphous metallic phase of a-Si:H; II—values of T_c of the crystallized phases of a-Si:H (filled circles); III—T_c of the nonequilibrium phase of a-Si:H. 1–10) Sequence of states of the same a-Si:H (10% H) sample up to the point of complete crystallization.

superconductivity at $P \lesssim 100$ kbar results from an increase in the concentration of the bcc phase, which is a semiconductor with a temperature dependence of the resistance which is typical of a semiconductor.

At intermediate pressures, $140 < P < 180$ kbar, preceding crystallization, we observe an interesting effect: A slight increase in the pressure causes a significant increase in T_c (up to ~ 3 K); curve III. The state with the higher T_c persists for 2–3 h at room temperature. After a long annealing, this state is disrupted, and the system goes into either an equilibrium metallic amorphous state (at $P < 160$ kbar) with critical temperatures corresponding to curve I or a crystalline state with T_c corresponding to curve II. We do not observe intermediate values of T_c between the "high-temperature values" and the equilibrium values. After a complete crystallization of the sample (at $P > 180$ kbar), this effect disappears.

The increase in T_c when the system goes into the nonequilibrium state near the threshold for structural stability (curve III) seems to be most closely related to the decrease in T_c observed in Ref. 3 for superconducting glasses during annealing near the glass transition point to values below T_c of freshly quenched samples in a nonequilibrium state. In certain cases, the change in T_c in those experiments reached 15%.

The significant increase in T_c of the a-Si:H films and of glasses in a nonequilibrium state near the crystallization threshold (or the glass transition point) is evidence that the electron-electron interaction responsible for the superconductivity is intensified in this state. The increase in the interaction energy in the electron system may be due to either an intensification of the ordinary electron-phonon interaction or the appearance of other, nonphonon, superconductivity mechanisms. One such mechanism that is presently being discussed is a virtual interaction of electrons with the tunnel levels which are characteristic of amorphous systems.[4–6]

However, according to theoretical estimates in Ref. 6, this mechanism would cause only a slight change in T_c (only a few percent). At present, we have no data of any sort which indicate, that there is a substantial change in the phonon spectrum of amorphous materials in a nonequilibrium state and that the electron-phonon interaction may be intensified in them. We thus do not rule out the possibility that the

increase in T_c near the crystallization threshold stems from the interaction of electrons with configurational excitations of another type, e.g., concentration waves.[7–8] A mechanism of this type, which is of a relaxation nature, as was shown in Refs. 7 and 8, may also be responsible for the high values of T_c of amorphous Ga and Bi films, the anomalies observed[9] in the properties upon crystallization, and the increase in T_c of extremely deformed samples of P (Ref. 10) and a-Si (Ref. 11).

We sincerely thank V. E. Egorushkin for a discussion of the results and D. P. Utkin for furnishing the samples.

[1]I. V. Berman, N. B. Brandt, V. A. Alekseev, I. E. Kostyleva, V. I. Sidorov, and O. P. Pyatkina, Pis'ma Zh. Eksp. Teor. Fiz. **40**, 472 (1984) [JETP Lett. **40**, 1303 (1984)].
[2]S. Minomura, Amorphous Semiconductors: Technol. Devices, 1981, p. 245.
[3]Z. Altounian, Tu Guo-hau, and O. Strom-Olsen, Solid State Commun. **40**, 221 (1981).
[4]P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. **25**, 1 (1972).
[5]W. A. Philips, J. Non-Cryst. Solids **31**, 267 (1978).
[6]R. Harris, L. J. Lewis, and M. J. Zuckermann, J. Phys. F **13**, 2323 (1983).
[7]S. V. Alyshev, V. E. Egorushkin, and A. I. Kul'ment'ev, Dokl. Akad. Nauk SSSR **258**, 7 (1981).
[8]V. E. Egorushkin, A. I. Murzashev, and V. E. Panin, Izv. Vyssh. Uchebn. Zaved., Fiz. No. 1, 15 (1984).
[9]B. I. Belevtsev, N. B. Brandt, and Yu. F. Komnik, Pis'ma Zh. Eksp. Teor. Fiz. **22**, 510 (1975) [JETP Lett. **22**, 249 (1975)].
[10]H. Kawamura, I. Shirotani, and K. Tachikawa, Solid State Commun. **49**, 879 (1984).
[11]T. V. Valyanskaya, G. N. Stepanov, and E. N. Yakovlev, Trudy XXIII Vsesoyuznogo soveshchaniya po fizike nizkikh temperatur (Proceedings of the Twenty-Third All-Union Conference on the Physics of Low Temperatures), Part I, 1984, p. 112.

Translated by Dave Parsons