

# A typical example of metastability: Metallic glasses

Pol Duwez

*Professor Emeritus of Applied Physics and Materials Science, California Institute of Technology, Pasadena, California 91125*

(Received 29 December 1982; accepted 7 February 1983)

The general term metallic glasses is now generally accepted to define a class of amorphous alloys obtained by rapid solidification from the liquid state. This definition corresponds exactly to the definition of a glass in general, except that in the case of well known silicate glasses the liquid does not require a rapid rate of cooling to prevent crystallization, and that is not the case for metallic glasses. The first metallic glass, an alloy of gold and silicon, was synthesized at Caltech in the summer of 1959. During the last 20 years, the interest in metallic glasses has increased steadily. There is still widespread interest in both theoretical and experimental studies of metallic glasses. About 10 years ago the potential importance of metallic glasses as a class of new materials with unusual physical properties was recognized by industry. It will take a long time before production of metallic glasses can be measured in tons, but it is encouraging to see that an increasing number of industrial research centers are involved in studies of metallic glasses.

PACS numbers: 64.60.My, 74.70. — b, 72.15.Cz, 75.50.Kj

## I. INTRODUCTION

This meeting is almost exclusively devoted to semiconducting materials and since I have been concerned with metals almost exclusively I do not feel really at home. However, the theme of the meeting being metastability covers all types of atomic bonds in solids. Metastability has always been of great interest to metallurgists and I think it is becoming important also in semiconductors, as evidenced by the attendance at this meeting. The most useful metals (which are actually not pure metals but alloys) are steel and aluminum, which are both metastable. The iron-carbon phase diagram which is used for describing the structure of ordinary steels is actually a metastable diagram between iron and the metastable compound cementite ( $\text{Fe}_3\text{C}$ ). The aluminum alloys airplanes are made of, essentially aluminum-copper alloys, are purposely made nonequilibrium in order to increase their strength. I will not attempt to remind you of the thermodynamic meaning of metastability, since you are all familiar with what it means in your own field of interest, so let me directly go to the main subject of this introductory lecture, namely, metallic glasses.

By definition a glass is a solid material obtained from a liquid which does not crystallize during solidification, and is therefore an amorphous solid. The glass is metallic when it contains enough metal atoms so that its physical properties, such as electrical and thermal conductivities, are similar to those of a crystalline material of the same composition. Contrary to the familiar silicate glasses which are amorphous even under very slow cooling rates, metallic glasses require cooling rates of at least  $10^5$  °C/s. Several techniques are now in use to produce metallic glass specimens in laboratories. They are all based on the same basic principles which guided the design of the first successful quenching experiment at Caltech in 1960, when an amorphous metallic alloy (80 at. % Au 21% Si) was obtained. In all of them, a thin layer of molten alloy is cooled by conduction onto a copper substrate. Progress has been made in increasing the size of the

quenched specimens from a few square centimeters to strips up to 10 cm or more in width and practically infinite lengths, a method generally referred to as melt spinning. Amorphous alloys have been known for many years, although they were not recognized as such. In a paper by Brenner and Riddell,<sup>2</sup> reference is made to a publication of Wurtz in 1845, which described a method for obtaining a nickel deposit on iron by chemical decomposition of a Ni solution with hypophosphide. From the details given in this paper, it is most likely that the metallic deposit was amorphous, but no evidence for that could have been given 65 years before the discovery of the diffraction of x rays by crystalline lattices. Very few applications were found for the electrodeposited amorphous nickel. This is not true for two other methods for preparing amorphous films, namely vapor deposition and sputtering. Vapor deposition on a very cold substrate (liquid helium range) is the only successful method for preparing pure amorphous metals. The resulting films, however, are very unstable and crystallize around 30 or 40 K. Alloys containing several metals or metals and metalloids can also be vapor deposited on room temperature substrates and are quite stable. Thin films obtained by sputtering are generally more stable than vapor deposited ones, and that is one reason why they are widely used in making semiconducting devices. Finally, amorphous structures may be obtained by subjecting a crystalline solid to a heavy dose of radiation. This problem is closely related to that of the highly disordered structures found in ion implanted semiconductors. Although the implanted regions are highly disordered, it is not clearly established that they are really amorphous: The very thin layer of implanted material renders difficult the interpretation of the observed diffraction effects.

## II. STRUCTURE OF METALLIC GLASSES

In spite of the absence of a long range periodicity, which is the essential property of a crystal, the structure of a metallic glass as well as that of a silicate glass or of a liquid alloy is defined by the local order in a group of atoms involving the

first, second, and the third neighbors of any given atom. Such structures have been studied for a long time in connection with liquid and amorphous solids such as silicate glasses and chalcogenides. The techniques used for these studies involve scattering of either x rays, electrons, or neutrons. Additional information can be gained from Mössbauer experiments and more recently from the fine structure of the x-ray absorption edge of the alloys. The x-ray diffraction method is certainly the most convenient one and is the most widely used.

The results of the scattering experiments do not give by themselves a description of the atomic arrangement. To solve this problem it is necessary to assume a certain model for the packing of the atoms in the structure. The dense random packing (DRP) of hard spheres is the most widely accepted model to describe the structure of metallic glasses. This model, first proposed by Bernal<sup>3</sup> who applied it to liquids, has been and still is the basic concept on which all the (DRP) models are based. The DRP model gives a quite accurate description of the structure of amorphous solids containing only one kind of atom. Most metallic glasses, and especially those which are now under consideration for practical applications, contain at least two kinds of atoms of different atomic size, and in some cases as many as seven. In addition, some of the atoms may be semimetals with a somewhat covalent type of bonding. Building up a satisfactory model is not just packing atoms of different sizes at random. Since the properties of metallic glasses depend mostly on the short range order, it is very important to carefully select the initial cluster of a critical number of atoms which then serves as a motive which repeats itself to fill space without being systematically translated in three directions. The choice of the packing in the original cluster is guided by the results of scattering experiments.<sup>4</sup>

### III. ELECTRICAL RESISTIVITY

The two important characteristics of the electrical conductivity of metallic glass are (1) their resistivity is relatively high, greater than  $100 \mu\Omega \text{ cm}$  at room temperature, (2) their temperature coefficient is very small and can be zero or negative (in the range of  $\pm 10^{-4} \text{ K}^{-1}$ ). The combination of these two properties leads to a very high residual resistivity at 0 K. The high resistivity of amorphous alloy compared with that of the same alloy in the crystalline state is related to the increased scattering of the conduction electrons due to a random atomic arrangement. In such a random structure, the phonon contribution to the scattering of electrons is small, hence the small temperature coefficient of resistivity. The high value of resistivity combined with a very small temperature coefficient might be of interest in some electrical circuitry of measuring instruments requiring resistance components insensitive to temperature.

Many metallic glasses have a negative coefficient of resistivity. In that case it is sometimes possible to change the coefficient from negative to positive by a change in the composition of the alloy. This is the case for ternary alloys Pd-Ni-P. In alloys containing equiatomic concentrations of Pd and Ni, the coefficient progressively changed from a positive to a negative value with P concentrations increasing from 15

to 27 at.%, as shown in Fig. 1. The alloy containing about 24 at.% has a zero temperature coefficient, and this remains true in a wide temperature range from 20 to about 460 K. A negative temperature coefficient of resistivity is not unusual and has been found in a number of crystalline alloys as, for example,  $\text{Ti}_{67}\text{Al}_{33}$ ,  $\text{Ti}_{80}\text{Ni}_{20}$ , and  $\text{Zr}_{70}\text{U}_{30}$ . Theories have been proposed to explain the negative coefficient of resistivity of metallic alloys.<sup>5</sup> It has been observed that a negative coefficient is likely to exist when the room temperature resistivity of the alloy is greater than about  $150 \mu\Omega \text{ cm}$ . This correlation first found for crystalline alloys is also valid in the case of metallic glasses Pd-Ni-P, Pt-Ni-P, and Pt-Cu-P.<sup>6</sup>

In a number of metallic glasses containing an atom having a magnetic moment there is a resistivity minimum at low temperature, this is characteristic of the Kondo effect found in a number of crystalline alloys. The minimum in resistivity in metallic glasses, however, does not follow the classical Kondo theory, but since it is also due to an interaction between the *s* electrons of the host matrix and the *d* electrons of the magnetic impurity, it could be called a "Kondo-like" effect. The most interesting amorphous matrix in which a magnetic impurity can be dissolved is a Pd-Si alloy quenched from the liquid state. A systematic study of the effect of Co, Fe, Cr, and Mn substituting for Pd in  $\text{Pd}_{80}\text{Si}_{20}$  was published in a series of papers. The maximum concentration of these atoms was limited because above a certain concentration (11 at.% for Co and 7 at.% for Fe, Cr, and Mn), it is not possible to retain an amorphous phase. Within these ranges of concentrations, the temperature of the resistivity minimum increased linearly for Co, Cr, and Mn and remained approximately constant for Fe. The increase in the resistivity minimum temperature with concentration of the magnetic impurity is particularly large for Cr for which  $T_m$  is approximately 500 K for 7 at.% Cr<sup>7</sup> (Fig. 2). Because of the rapid rise in resistivity below 150 K, the  $\text{Cr}_7\text{Pd}_{73}\text{Si}_{20}$  has been

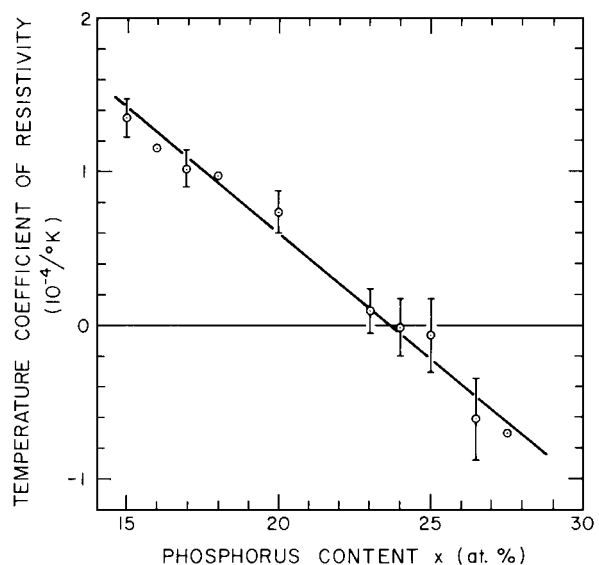


FIG. 1. Variation of the temperature coefficient of resistivity at room temperature with phosphorus content  $x$  in  $(\text{Pd}_{50}\text{Ni}_{50})_{100-x}\text{P}_x$  glassy alloys (Ref. 18).

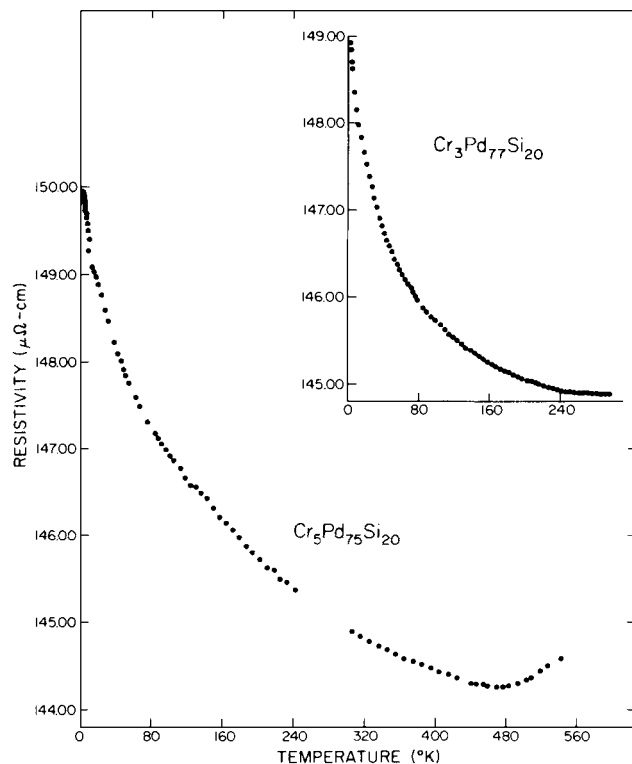


FIG. 2. Electrical resistivity vs temperature for two glassy CrPdSi alloys (Ref. 7).

suggested as an attractive metallic resistance thermometer.<sup>8</sup> Its sensitivity is around  $60 \mu\text{V K}^{-1}$  at 10 K.

#### IV. MAGNETIC PROPERTIES

The existence of ferromagnetism is not limited to crystalline alloys. As early as 1950, Ni-P alloys containing from 10 to 17 at. % P obtained by electroless deposition were weakly ferromagnetic. Their amorphous structure was suggested at that time and was definitely confirmed in 1964.<sup>9</sup> The first strongly ferromagnetic metallic glass was  $\text{Fe}_{70}\text{P}_{15}\text{C}_{10}$  reported in 1967.<sup>10</sup> The Curie temperature is around 320 °C, about 70 °C below the temperature at which the alloy crystallizes rapidly. The ferro to paramagnetic transition is very sharp and this was confirmed by Mössbauer spectroscopy measurements which gave a Curie temperature of  $313 \pm 2$  °C. The average field versus temperature curve follows essentially a Brillouin function with  $J = 1$ . From bulk magnetization measurements the magnetic moment per Fe atom is  $2.10 \pm 0.01 \mu_B$  compared with  $2.22 \mu_B$  for pure crystalline Fe. The hysteresis cycle is typical of a soft ferromagnet with coercive force of about 3 Oe. Many new ferromagnetic glasses have been prepared during the last 15 years, and the coercive force of some of those new materials is as low as a few milli-Oersteds.

The analogy between Fe and Ni suggested a study of Ni-P-C ternary alloys but the results were negative and amorphous Ni-P-C alloys cannot be obtained by liquid quenching. It is possible, however, to replace 50% of the Fe by Ni in glassy  $\text{Fe}_{75}\text{P}_{15}\text{C}_{10}$ .<sup>11</sup> The low temperature resistivity and the Curie temperature were measured in  $(\text{Fe}_{100-x}\text{Ni}_x)_{75}\text{P}_{15}\text{C}_{10}$  with  $x$  varying from 0 to 50. The resistivity-temperature curve, as in the case of Fe-P-C, has a shallow minimum in

the range of 20–30 K. The Curie temperature increases slowly with increasing Ni content and has a maximum at  $x = 20$ . These results could be fitted to a theoretical curve obtained by a coherent potential approximation method<sup>12</sup> with exchange integrals  $J_{\text{Fe-Fe}} = 1$ ,  $J_{\text{Fe-Ni}} = 1.2$ , and  $J_{\text{Ni-Ni}} = 0$ . By analogy also, Mn-P-C alloys were quenched, expecting these alloys to be antiferromagnetic. This was confirmed but contrary to Fe-P-C,  $\text{Mn}_{75}\text{P}_{15}\text{C}_{10}$  amorphous alloys are extremely brittle and break up into small flakes less than 5 mm wide. It was, therefore, not possible to measure electrical properties, but the samples were suitable for magnetic measurements. The amorphous structure of the alloy was demonstrated in a study of the radial distribution function.<sup>13</sup> Since Fe and Mn are completely soluble in each other, at least at high temperature, it was expected that alloys  $(\text{Fe}_{100-x}\text{Mn}_x)_{75}\text{P}_{15}\text{C}_{10}$  would be amorphous for  $x$  varying from 0 to 100, and this was found to be the case.<sup>14</sup> The temperature and field dependence of magnetization of these alloys were studied from 4.2 to 300 K and in fields varying from 1 to 8.5 kOe. On the Fe-rich side (Mn 40%), the alloys are ferromagnetic and at 4.2 K, the moment on Fe atoms decreases linearly from  $2.07 \mu_B$  to  $0.22 \mu_B$  for  $(\text{Fe}_{60}\text{Mn}_{40})_{75}\text{P}_{15}\text{C}_{10}$ . The magnetic structure of alloys with  $x = 50$ –100 is complex. These alloys are characterized by a peak in the magnetization curves at temperatures between 15 and 40 K and a ferromagnetic-type curvature in the Curie-Weiss plots. This behavior was tentatively explained by the existence of ferromagnetic-like regions with partially compensated spins and other antiferromagnetic localized regions.

The first generation of liquid quenched amorphous magnetic alloys containing Fe, P, and C became the prototype of practically all the ferromagnetic metallic glasses reported to date. The number of glassy alloys containing the 3d transition metals Cr, Mn, Fe, Co, and Ni and high valence elements generally referred to as glass formers (B, C, Si, and P) increased rapidly when attention was given to alloys containing more than three elements. First, B was substituted for either P or C in the already known Fe-P-C and Ni-P-C alloys and  $\text{Fe}_{76}\text{B}_{17}\text{C}_7$ ,  $\text{Ni}_{75}\text{P}_{15}\text{B}_{10}$ , and  $\text{Co}_{73}\text{P}_{15}\text{B}_{12}$  quenched from the liquid state were found to be amorphous.<sup>15</sup> Second, glassy alloys containing as many as six elements were quenched from the liquid state. A general formula for all those alloys can be written  $T_{70-80}G_{30-20}$ , where  $T$  stands for the sum of the 3d transition metals and  $G$  includes the sum of the glass formers. Several of these complex alloys contained up to 5 at. % Al which is believed to act as Si in enhancing the stability of the amorphous state. From that point of view, Al could be considered as a glass former, similar to B. With such a flexibility in formulating the composition of metallic glasses, it is not surprising that most of the magnetic properties of crystalline alloys can be duplicated and very often improved.

Since the disordered structure of metallic glasses is apparently isotropic, these materials should be magnetically isotropic. In general, this is not the case. Liquid quenching introduces internal stresses and this may be one of the reasons for their anisotropy. An appropriate heat treatment at a low enough temperature to avoid crystallization can drastically reduce internal stresses. But even in that case magnetic an-

isotropy may exist on an atomic scale. In a disordered structure a magnetic atom is subjected to a nonuniform electric field produced by the neighboring atoms and the magnitude, and the direction of the magnetization axis vary from one atom to the other. As a result, spins can be aligned within a certain critical volume which is, therefore, a magnetic domain. Such domains are separated by domain walls which have been observed in electron microscopy.<sup>16</sup>

From the point of view of industrial applications, the most interesting property of metallic glasses is their small coercive force which results in very low hysteresis losses in transformer cores. With improving technology, the cost of metallic glasses in sheet form should be relatively low since they are obtained directly from the liquid state in one single operation, thus avoiding very costly and power consuming operation of forging and rolling. Some critical magnetic properties of metallic glasses however should be improved, especially their magnetic saturation and their Curie temperatures, which are still relatively low.

## V. SUPERCONDUCTING PROPERTIES

In the various theories of superconductivity in metals and alloys, the existence of a crystalline lattice is not assumed. The approach to finding a suitable composition for such a metallic glass was to start with a superconducting metal and find an alloying element susceptible of forming a glass by liquid quenching. The search was then focused on a binary system based on a superconductor and an alloying element forming a low melting point eutectic with the superconductor. These conditions are satisfied in the La–Au system and it was found that these alloys can be liquid quenched into an amorphous phase between 16 and 24 at.% Au. The La<sub>80</sub>Au<sub>20</sub> alloy has a transition temperature of 3.5 K. The transition is very sharp, with a width of about 0.03 K. The number of superconducting metallic glasses reported so far is about 12.

The transition temperatures of the glassy superconductors reported so far (less than 9 K) is much lower than those of crystalline alloys which are as high as 23 K. It does not seem impossible, however, that new superconducting glasses will not be found in the future. The theory of superconductivity does not predict that the absence of a crystalline lattice will automatically lead to a low transition temperature. In order to make a meaningful comparison between the amorphous and the crystalline state, it is necessary to obtain an amorphous alloy composition such that when crystallizing at high temperature, its structure consist of single crystalline phase. This is not possible so far since the compositions of the glassy superconductors known today are complex and consist of two phases or more when they crystallize into their equilibrium structure. In such a comparison between the su-

perconducting properties of the amorphous and crystalline alloys is difficult if not impossible.

A property which is definitely associated with the absence of a crystal lattice in glassy superconductors is their sensitivity to magnetic fields and high current densities. The conduction electron scattering in highly disordered structures is very high, and this results in a high electrical resistivity and a very small mean free path. For example, the residual resistivity of La<sub>78</sub>Au<sub>22</sub> is about 200  $\mu\Omega$  cm and the electron mean free path is of the order of magnitude of interatomic distances. As a result the coherence length in the superconducting state is small (typically 30 to 100 Å) the depth of penetration is relatively large (2000 to 10 000 Å), and as a consequence the Ginzberg–Landau parameter is large, in the range of 40 to 100.<sup>17</sup> Metallic glasses are, therefore, strong type-II superconductors.

In superconducting glasses the disorder in the atomic structure is on a scale much smaller than the coherence length. As a consequence, there is practically no pinning centers for the magnetic flux, and the critical current decreases very rapidly with an applied magnetic field. The inherent characteristic of amorphous superconductors might seriously limit their application to superconducting power transmission lines and high flux magnets. This problem is probably not insoluble. It may be possible, for example, to introduce pinning centers in an amorphous alloy by a suitable thermal treatment which would result in fine crystalline precipitates having the required critical size and spaced at a critical distance to maximize the flux pinning effect. This problem is essentially a metallurgical problem which does not seem impossible to solve. In fact, some preliminary results have already been obtained in that direction.

<sup>1</sup>W. Klement, Jr., R. H. Willens, and Pol Duwez, *Nature* **186**, 869 (1960).

<sup>2</sup>A. Brenner and G. Riddell, *J. Res. Natl. Bur. Stand.* **37**, 31 (1946).

<sup>3</sup>J. D. Bernal, *Nature* **185**, 68 (1960).

<sup>4</sup>G. S. Cargill III, *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1975), Vol. 30. p. 227.

<sup>5</sup>F. Brouers and M. Brauwiers, *J. Phys. Paris* **36**, L17 (1975).

<sup>6</sup>G. L. Tansonan, *Phys. Lett. A* **54**, 307 (1975).

<sup>7</sup>R. Hasegawa and C. C. Tsuei, *Phys. Rev. B* **2**, 1631 (1970).

<sup>8</sup>C. C. Tsuei and Pol Duwez, *J. Phys. E* **4**, 466 (1971).

<sup>9</sup>J. Dixmier, K. Doi, and A. Guinier, *Physics of Non-Crystalline Solids—Proceedings of the International Conference* (Interscience, New York, 1964), p. 67.

<sup>10</sup>Pol Duwez and S. C. Lin, *J. Appl. Phys.* **38**, 4096 (1967).

<sup>11</sup>R. Hasegawa and J. A. Dermon, *Phys. Lett. A* **42**, 407 (1973).

<sup>12</sup>E.-N. Foo and D.-H. Wu, *Phys. Rev. B* **5**, 98 (1972).

<sup>13</sup>A. K. Sinha and Pol Duwez, *J. Appl. Phys.* **43**, 431 (1972).

<sup>14</sup>A. K. Sinha, *J. Appl. Phys.* **42**, 338 (1971).

<sup>15</sup>K. Yamauchi and Y. Nakagawa, *Jpn. J. Appl. Phys.* **10**, 1930 (1971).

<sup>16</sup>D. I. Paul, J. Marti, and L. Valadex, *AIP Conference Proc. No. 18 on Magnetism and Magnetic Materials* (AIP, New York, 1974), p. 1377.

<sup>17</sup>B. M. Clemens, W. L. Johnson, and J. Bennett, *J. Appl. Phys.* **51**, 1116 (1980).

<sup>18</sup>A. K. Sinha, *Phys. Rev. B* **1**, 4541 (1970).