

Superconducting Phosphorus

Abstract. *Phosphorus, the element itself, becomes superconducting near 4.7°K and at pressures exceeding 100 kilobars. This constitutes one of the four last missing links in the proof that superconductivity is normal behavior for every truly metallic sp element. The three remaining ones are arsenic, sulfur, and iodine.*

At high pressures, red phosphorus will transform into a denser solid modification. This transformation has been found by Bridgman in his volumetric work in the neighborhood of 85 kb (1). Under shear stress, this transformation is observed at much lower pressures (2). After the pressure is released, red P is irreversibly transformed into the orthorhombic semiconducting black P modification.

Structural transformations of black P at high pressure have been investigated by Jamieson (3). He found two transitions under increasing pressure. Black phosphorus will transform first into an A7 lattice, which is the rhombohedral modification of As, Sb, and Bi under normal pressure and of Te above 15 kb (4). Once their A7 modifications transform at higher pressures, Sb, Bi, and Te become superconducting. Where-

as most of these high-pressure modifications have not yet been fully explored, it is known, however, that black P in the A7 modification will become simple-cubic in the vicinity of 110 kb (3). We expected, therefore, that at this pressure P will become superconducting, and we have now verified our hypothesis. In our pressure range, as of today, no similar polymorphic transformation for As has been observed.

The experimental details concerning the high-pressure electrical resistance cell have been described (5), and no major modifications were introduced. An important improvement of the former experimental high-pressure-low-temperature technique was achieved by using a small mechanically operated press which can be cooled down to liquid He temperatures. The load capacity of this press is about 10 to 12 tons, enough to reach a maximum pressure of 200 kb in the Drickamer scale (lead transition at 160 kb). The advantage of a press which can be cooled down to liquid helium temperature is obvious. The former technique suffered from the disadvantage that the thrust must be maintained by a clamping device which cannot be controlled in a very reproducible manner.

Temperatures above the boiling point of liquid helium can now be measured with high accuracy by surrounding the whole press with a screen of high thermal-conductivity copper and by varying the position of the press over the helium bath (6).

The phosphorus samples used were red P, from different lots; the purity was greater than 99.999 percent (7). Red phosphorus at pressures below 70 to 80 kb is an insulator with resistivities far above 10 megohms. This pressure value cannot be given with any considerable accuracy in that no internal pressure standard was used in these experiments. But the value agrees roughly with Bridgman's result that red P does not transform to a black modification up to about 85 kb under nearly hydrostatic conditions and normal temperatures. Upon further increase of pressure, the resistivity decreases gradually and suddenly drops sharply by several orders of magnitude to a final value which is typical for a metallic sample of the same geometrical dimensions (Fig. 1). There is a strong continuous drift of the resistance with time during the transformation to the metallic state. The same resistive transition has been observed by Harris *et al.* (8). An estimate of the pressure at which the steep resistance drop occurs gives a value in the vicinity of 110 kb. It is very likely, therefore, that the cubic high-pressure modification of P reported by Jamieson has been formed. At present it is difficult to decide whether the transformation of red

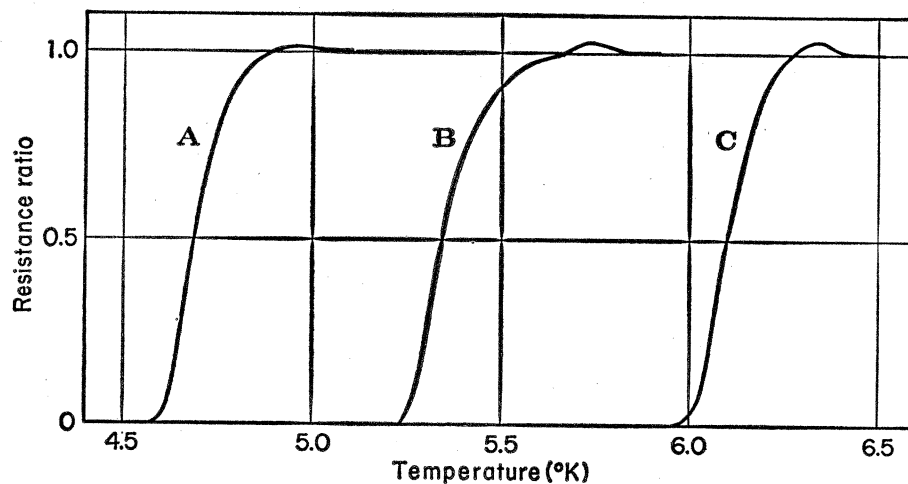
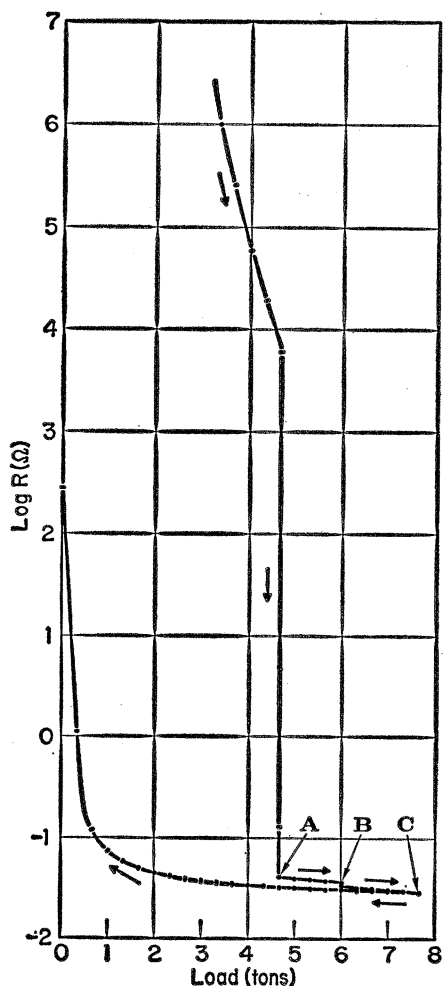


Fig. 1 (left). Room-temperature resistance of red phosphorus against pressure load. When the pressure is released, semiconducting black P is formed. Fig. 2 (above). Superconducting transition curves of the high-pressure metallic phase of phosphorus at three different pressures, thus indicating a large increase in transition temperature with pressure. The resistance is normalized to the residual resistivity in the normal conducting state.

P into metallic P involves a substantial intermediate formation of the A7 phase.

When starting from point A (Fig. 1) the sample is cooled down to low temperatures under constant load; the sample becomes superconducting with a rather sharp transition at about 4.7°K. This transition temperature corresponds reproducibly to the precipitous drop of the electrical resistance. If the pressure is increased at room temperature in two steps to points B and C in Fig. 1, the room-temperature resistance shows only a small further decrease. The superconducting transition temperature, however, is shifted to much higher values, as shown in Fig. 2. The monotonic increase with pressure indicates a pure pressure effect rather than any new crystallographic phase change. Thus it appears that P is the first nontransition metal to show a large positive pressure coefficient of T_c .

The low-temperature resistivity of all samples was about one-half of the room-temperature resistance, thus indicating a rather imperfect and strained lattice for the superconducting polymorph. After complete release of pressure, the resistance of the sample was about four orders of magnitude higher than in the metallic state (Fig. 1). This value is to be expected from the specific resistivity of semiconducting black P. In addition, the black color of the sample and the negative temperature coefficient of the resistance down to 1.2°K are convincing proofs that black P has been formed irreversibly on the pressure-releasing cycle.

The onset of superconductivity in P may depend on the prior history of the sample, and at the same time there may be more than one superconducting modification of P. But apart from these questions, the discovery of superconductivity in P is further proof that every truly metallic *sp* element will be found to be superconducting (9).

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Concentration-Gradient-Driven Convection: Experiments

Abstract. Concentration-gradient-driven convection was studied by measurement of the rate of dissolution of the lower face of a KCl single crystal in contact with various solvents. The rate of mass transfer due to convective stirring appeared to follow the Rayleigh number to the one-third power law. A regular pattern of etch pits due to the convective stirring action was observed in the crystal face after exposure to water for 5 minutes. Schlieren photographs of the early stages of dissolution showed a regular pattern of spikes having approximately the same dimensions as the etch pits in the crystals.

Differences between salt rejection in unstirred hyperfiltration systems (1), when membranes are placed above feed solutions and when membranes are placed below feed solutions, indicated marked differences in concentration polarization with orientation. The difference was attributed to stirring that arose from the density gradients formed near the interface where salt is rejected.

Natural-convection stirring of horizontal fluid layers is common (2, 3) when an adverse density gradient is produced by heating of a fluid from below. The enhancement of the rate of heat transfer between two horizontal solid surfaces by natural-convection stirring has been studied experimentally (2, 4, 5) and theoretically (6). These studies show that the Nusselt number for heat transfer (the dimensionless heat-transfer rate) N_{Nu} is a function of the Rayleigh number N_{Ra} :

$$N_{Nu}/(N_{Nu})_0 = C (N_{Ra})^n \quad (1)$$

where $(N_{Nu})_0$ is the Nusselt number in the absence of natural-convection stirring. For Rayleigh numbers greater than 20 times the critical, the value of n is $1/3$ and C is about 0.089. It is of interest to note that shear flow apparently has little effect on either the critical Rayleigh number (1) or the increase in Nusselt number due to natural-convection stirring.

A related stability problem occurs when two different fluids, having a common plane boundary, experience an acceleration in a direction perpendicular to their interface (8). When the acceleration is directed from the less-dense to the denser medium, the interface becomes unstable; as the instability

develops, the denser fluid jets out in long spikes.

Little is known about the effect of concentration-gradient-driven natural convection on the rate of mass transfer at a liquid-solid interface. Since such stirring was believed (1) to be responsible for the effect of orientation on the differences in rejection in the hyperfiltration experiments, we chose to study concentration-gradient-driven convection by measuring the rate of dissolution of the lower surface of a single crystal of KCl in contact with solvent. Such a technique has the advantage of eliminating high-pressure systems and permitting visualization of flow, but has

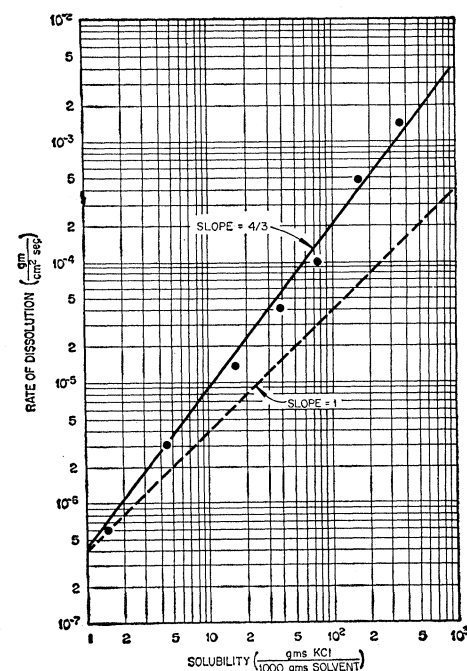


Fig. 1. The effect of solubility of KCl on rate of dissolution in ethanol-water solutions.