

## SUPERCONDUCTIVITY IN METASTABLE BISMUTH EUTECTIC ALLOYS

D. E. GORDON and B. C. DEATON

*Applied Research Laboratories, General Dynamics, Fort Worth, Texas*

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The superconducting transition temperature  $T_C$  has been measured in several bismuth eutectic alloys after exposure to 30 kbar pressure. It is found that the changes observed in  $T_C$  can be related to changes in the normal state resistivity of these samples.

In early high-pressure studies, Bridgman [1,2] observed metastable effects in several bismuth eutectic alloys and the irreversible production of new forms at pressures less than 30 kbar. The present investigation concerns a measurement of the superconducting transition temperature  $T_C$  of these new irreversible forms and a correlation between  $T_C$  and the normal state resistivity  $\rho$ . The specimens studied consisted of the following eutectic alloys: (1)  $\text{Bi}_{0.625}\text{Pb}_{0.375}$ , (2)  $\text{BiSn}$ , (3)  $\text{Bi}_{0.343}\text{In}_{0.657}$ , and (4)  $\text{Bi}_{0.86}\text{Tl}_{0.14}$ .

A conventional four-probe resistivity technique was employed for determination of the superconducting-normal transitions. The samples were prepared from 99.999% starting materials and were annealed for several weeks to remove all traces of strains as indicated from the sharpness of their superconducting transition curves. The alloys were subjected to high pressure in a piston-cylinder apparatus [3] and the compressibility of each monitored during pressurization.

The results of the superconductivity measurements are shown in table 1. These samples were

Table 1  
Change in superconducting transition temperatures due to high pressure treatment.

Composition	$T_C$	
	(Before high-pressure treatment)	(After high pressure treatment)
$\text{Bi}_{0.625}\text{Pb}_{0.375}$	8.05	7.25
$\text{BiSn}$	3.72	4.20
$\text{Bi}_{0.86}\text{Tl}_{0.14}$	6.50	6.50
$\text{Bi}_{0.343}\text{In}_{0.657}$	5.55	5.20

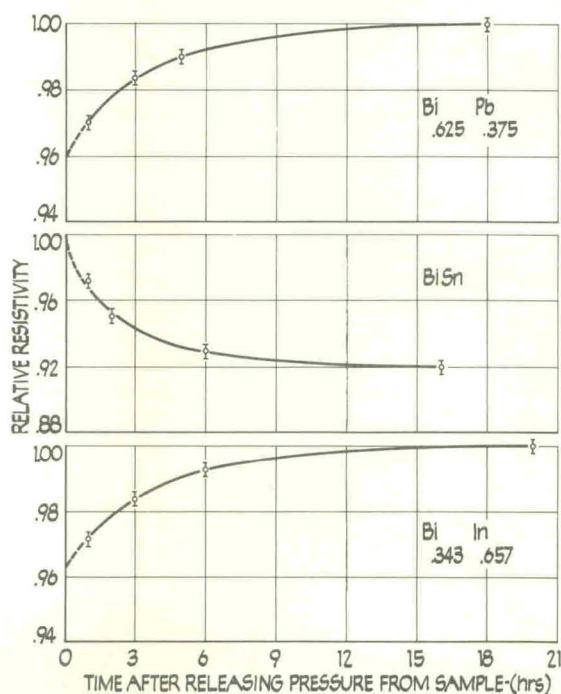


Fig. 1. Change in room temperature relative resistivity with time after releasing pressure of 30 kbar.

subjected to 30 kbar pressure at ambient temperature and their transition temperatures measured immediately after release of the pressure. It is seen from the results that the transition temperatures of  $\text{Bi}_{0.625}\text{Pb}_{0.375}$  and  $\text{Bi}_{0.343}\text{In}_{0.657}$  are decreased by the exposure to high pressure,  $T_C$  of  $\text{BiSn}$  is increased, and no change is observed in the case of  $\text{Bi}_{0.86}\text{Tl}_{0.14}$ .

If the pressurized samples were stored in liquid nitrogen, the values of  $T_C$  remained constant at the values indicated in the right-hand column

of table 1, while at room temperature,  $T_C$  changed with time, returning slowly to the value before pressing. It was observed that determination of the normal state resistivity of the samples served as an excellent indicator of this phenomenon as indicated in fig. 1. This close relationship between  $T_C$  and  $\rho$  is in line with the general trend that lower normal-state resistivity is associated with weaker superconductivity (lower  $T_C$ ) since both quantities depend on the strength of the electron-phonon interaction.

The following conclusions may be reached concerning the present experiments on the pressurization of Bi eutectic alloys: (1) The application of 30 kbar pressure induces transformation to new phases in  $\text{Bi}_{0.625}\text{Pb}_{0.375}$ , BiSn, and  $\text{Bi}_{0.343}\text{In}_{0.657}$ ; a fraction of the new phase is irreversibly trapped when the pressure is released as is indicated by X-ray diffraction patterns taken at 77°K immediately following release of pressure. The superconducting transition temperature of these samples is changed, the BiSn having a higher  $T_C$ , the  $\text{Bi}_{0.625}\text{Pb}_{0.375}$  and  $\text{Bi}_{0.343}\text{In}_{0.657}$  having a lower  $T_C$ . The presence of the new phases is indicated not only by changes in  $T_C$ , but by analogous changes in normal-state resistivity, in agreement with the general trend predicted by the BCS model of superconductivity. If these samples are allowed to remain at room temperature, thermal agitation provides sufficient energy to transform them back to the ori-

ginal phase; this change can be monitored quite satisfactorily by measuring the normal-state resistivity of the samples. (2) No change is observed in the transition temperature of  $\text{Bi}_{0.86}\text{Tl}_{0.14}$  exposed to 30 kbar pressure and no change in the normal-state resistivity was observed either. Evidently either the high-pressure phase was not metastable or the pressure needed to transform the material to the new phase was not reached. (3) On the basis of the present data and a compilation of previous results in the literature, it appears that there is a definite correlation between  $dT/dp$  and  $d\rho/dp$ , at least for non-transition elements and alloys. Ideally, then, a prediction of the change of  $T_C$  with pressure,  $p$ , for a new phase of a material could be made on the basis of a determination of  $d\rho/dp$  in the normal state at room temperature, which is a much simpler experiment. This prediction, of course, would be based on the assumption that the density of states  $N(0)$  does not change appreciably with pressure or at the phase transition.

#### References

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2. P. W. Bridgman, Proc. Am. Acad. Arts Sci. 82 (1953) 103; 84 (1955) 23; 84 (1955) 63; and 84 (1955) 80.
3. K. B. Ward Jr. and B. C. Deaton, Phys. Rev. 153 (1967) 947.

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