

REVIEWS OF MODERN PHYSICS

VOLUME 33, NUMBER 4

OCTOBER, 1961

Conclusions from Superconducting Molybdenum Technetium Alloys

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THE attempt to raise the transition temperature of superconductors dates back almost to 1911 when Kamerlingh Onnes discovered superconductivity in a mercury wire at 4.2°K.¹ The highest transition known today is that of Nb₃Sn at 18.05°K.² This progress over the last fifty years does not exactly encourage the hope for much higher temperatures in the near future. From the BCS theory³ one might expect transitions as high as one quarter of the Debye temperature, a limit nearer to 80°K than 20°K. But since Justi's discovery⁴ of a transition temperature of 15° for NbN, twenty years have passed and only three degrees have been gained though many hundreds of new superconductors have been discovered in that period. This paper reports new experiments that support a rather pessimistic outlook for any substantial further increase in transition temperatures. After Kunzler's discovery that superconducting magnets with fields in the 10⁵ gauss range will be feasible, it became extremely interesting to raise the transition temperatures. Even though the fields possible with superconductors are not proportional in a simple manner to their respective transition temperatures, the limits of the latter will essentially determine the limits on superconducting magnets.

It is quite obvious that the pure elements will be of no promise as the highest superconducting elements are niobium (8.8°) and technetium^{6,7} (8°–11°, 9.3°). Therefore, one has to rely upon intermetallic phases and com-

pounds. Two quite different crystal structures had appeared in the past to be most favorable for the occurrence of high superconductors. One was the NaCl lattice of the interstitial metallic compounds of which NbN was the best example at 15°K. NbC is superconducting at a lower temperature, namely 6°K. Solid solutions of the form Nb(C.N) reach a peak with the superconducting transition temperature at 17.8°K.⁸ The other structure favorable to superconductivity is the

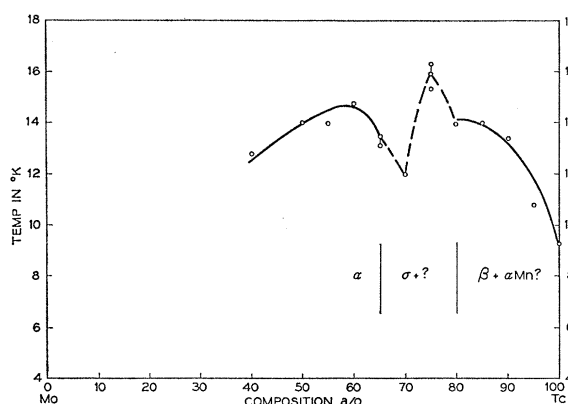


FIG. 1. Superconductivity in Mo-Tc System.

cubic β -W structure of intermetallic compounds, with its best example being Nb₃Sn at 18°K. Several isomorphous compounds such as V₃Si,⁹ V₃Ga,⁸ Nb₃Al,¹⁰ and Nb₃Ga⁸ have only slightly lower transition temperatures, that are within a degree or so from Nb₃Sn. The compounds mentioned so far involve chemical

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⁴ E. Justi and G. Zickner, Physik Z. **42**, 258 (1941).
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⁶ J. G. Daunt and J. W. Cobble, Phys. Rev. **92**, 507 (1953).
⁷ Author's measurements.

⁸ B. T. Matthias, E. A. Wood, E. Corenzwit, and V. B. Bala, J. Phys. Chem. Solids **1**, 188 (1956).
⁹ G. F. Hardy and J. K. Hulm, Phys. Rev. **93**, 1004 (1954).
¹⁰ E. Corenzwit, J. Phys. Chem. Solids **9**, 93 (1959).

bonds between transition *and* nontransition elements. Most experiments had been done on such systems since it was my belief that a partly covalent bond was necessary to achieve high superconducting transition temperatures. This generalization has now proved to be wrong by looking at technetium alloys.

Relatively high transition temperatures (12.5°K) of solid solutions of Re in Mo had been found by Hulm.¹¹ It seemed interesting, therefore, to investigate the superconducting behavior of Mo-Tc alloys. As these two transition elements (42 and 43) are direct neighbors in the periodic system, any bond would be expected to be very close in properties to the metallic bond of the pure element. The superconducting transitions in the Mo-Tc system are shown in Fig. 1. While the 16°K region at the technetium-rich side belongs probably to a phase which is a solid solution of Mo in Tc, the 15° temperatures are for solid solutions of Tc in the body-centered cubic molybdenum. They are ductile and of real promise for superconducting magnets. But at the same time the Mo-Tc alloys dash hopes for superconducting transition temperatures much above 18°K . While it seems quite probable that

more developed technetium metallurgy will gain one or two degrees, no drastic improvement in this system seems likely.

Thus the result emerges that ranging from pure metallic alloys with wide homogeneity ranges to intermetallic compounds with virtually no homogeneity range, from interstitial compounds to solid solutions, the maximum transition temperatures seem always to be between 16° and 18°K , regardless of the crystal structure or nature of the metallic bond.

This is so far a purely experimental fact. On the other hand, many compounds which seemed likely to exist from a chemical point of view and according to empirical rules¹² would have had higher transition temperatures, could not be synthesized until now. Thus we face the question whether it is lack of metallurgical skill or laws of nature unknown to us which prevent the existence of higher superconducting transition temperatures. This would mean that with 18°K one has come close to the theoretical limit if there is such a thing.

Many thanks are due P. W. Anderson, T. H. Geballe, and P. A. Wolff for encouraging discussions.

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¹² B. T. Matthias, Phys. Rev. **97**, 74 (1955).