PHYSICAL REVIEW VOLUME 92, NUMBER 4 NOVEMBER 15, 1953

Transition Temperatures of Superconductors

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(Received August 3, 1953)

Superconductivity has been found in a number of new compounds between the non-superconducting transition elements and nonmetals such as Si, Ge, and Te. These findings have suggested possible criteria for superconductivity in both elements and compounds.

INTRODUCTION

As has been pointed out before,[1] the superconducting elements lie in two distinct groups in the periodic system. Mo, W, and Bi border on these groups; although not superconducting themselves, they form many superconducting compounds.[2] Bismuth itself, when condensed below 20°K is a superconductor.[3]

Plotting the atomic volumes of the elements *versus* their atomic number, Clusius[4] found small atomic volumes for most superconductors. However, an equal number of non-superconductors fall in that same range of atomic volumes and the correlation is therefore not very satisfactory.

Fröhlich's and Bardeen's criteria are based on their now well-known theories of the lattice-electron interaction.[5,6] They contain the electrical conductivity, its temperature coefficient and the sound velocity and represent beyond any doubt the qualitative distinction between superconductors and non-superconductors. These theories offer also an interpretation of the isotope effect,[7] according to which for a series of superconducting isotopes the transition temperature varies inversely with the square root of the atomic mass:

$$T_c \propto 1/\sqrt{m}.$$

Although Bardeen does not mention compounds, Fröhlich suggests the investigation of the Au–Pd system. This is based on his calculation of an optimum number of free electrons in the superconducting phase. Magnetic measurements on Au–Pd alloys had shown that it was possible to vary this number by gradually filling the *d* shell of Pd. Neither Au nor Pd are superconducting, and as in former investigations all but one[8,9] superconducting compound of non-superconducting elements had contained either Mo, W, or Bi, the Au–Pd system was chosen as the starting point of our investigation of the superconducting compounds of non-superconducting elements.

NON-SUPERCONDUCTING COMPOUNDS

A range of binary alloy compositions with Au, Ag, or Cu as one element and Pd or Pt as the other were investigated. For those compositions in which a superlattice had been reported, the samples were annealed for three months. None of them gave any indication of superconductivity above 1°K.

Susceptibility measurements in the $MgCu_2-MgZn_2$ system had indicated a strong variation of the number of free electrons with change in relative composition.[10] This whole system was now investigated. No superconductivity above 1°K was detected in $MgCu_2$, $MgZn_2$ or any of eight intermediate alloys. Negative results were obtained as well for Au–Be and Pd–Be systems. These together with previous[1] negative results suggested that this approach was not likely to be fruitful.

SUPERCONDUCTING COMPOUNDS

Most of the previously investigated alloys and compounds had been truly metallic, distinguished by their rather small ratio of valence electrons/atom$=R$. In most cases $R<2$. (This is a good criterion for a pure metallic bond according to Schubert.)[11] It was noticed also that the elements, with the exception of Zn and Cd which are superconductors, all had more than two valence electrons/atom. Therefore a study was begun of compounds for which $R>2$. (Again according to Schubert[11] this implies that the predominant metallic bond has become partly replaced by an ionic or covalent bond.[12]) This approach proved more successful as we will indicate below.

The $[CaF_2]$ crystal structure class, although usually

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[1] B. T. Matthias and J. K. Hulm, Phys. Rev. **87**, 799 (1952).

[2] The superconducting Mo compounds observed heretofore contain a nonmetal such as B, C, N, Si, and Ge as the other partner. Relying on rules to be discussed, a more metallic compound Mo_3Sb_4 was prepared and found to become superconducting at 2.1°K.

[3] R. Hilsch, Oxford Conf. Low Temp. 119 (1952).

[4] K. Clusius, Z. Elektrochem. **38**, 312 (1932).

[5] H. Fröhlich, Phys. Rev. **79**, 845 (1950).

[6] J. Bardeen, Phys. Rev. **80**, 567 (1950).

[7] E. Maxwell, Phys. Rev. **78**, 417 (1950); C. A. Reynolds *et al.*, Phys. Rev. **78**, 487 (1950).

[8] The exception was CuS.

[9] W. Meissner, Z. Physik **58**, 570 (1929).

[10] Witte, Klee, and Lieser, Naturwiss. **38**, 185 (1951).

[11] K. Schubert, Z. Metallkunde **41**, 418 (1950).

[12] According to most theories the conduction electrons are the carrier of the supercurrents in the superconducting state. As their number is not always easily determined and, as will be shown later on, a connection between superconductivity and the number of *valence* electrons/atom can be more readily obtained, we will continue to consider the number of valence electrons/atom. The connection between valence electrons and conduction electrons is by no means obvious. For instance Nb and Bi both have 5 valence electrons/atom, but Nb is a good metal and a superconductor in contrast to Bi. The detailed band structure is of course a decisive factor. Bi condensed below 20°K becomes a superconductor, probably in a cubic modification (see reference 3).

considered typically ionic, contains a certain number of intermetallic compounds. In this class $CoSi_2$ has been found to become superconducting.[13] While it may be difficult to define the number of valence electrons for cobalt, it is safe to assume $R(\text{cobalt}) \geqslant 2$, therefore, $R(CoSi_2) \geqslant 3.3$. Other isomorphous intermetallic compounds have thus far not been found to become superconducting above 1°K. They are shown in Table I.

It is likely from a consideration of either electrons or holes in an incompleted d shell that the R's of the nonsuperconducting compounds are no larger in any case than $R(CoSi_2)$. For most of the remaining intermetallic compounds in this $[CaF_2]$ structure $R=8/3$ which, according to Mott and Jones, is the number of electrons required to fill a Brillouin zone.[14] It is therefore understandable why compounds like Mg_2Si which have values of R so close to those for a filled zone are not superconductors but semiconductors. One may therefore expect superconductivity in the $[CaF_2]$ structure for compounds whose $R > 2$ but at the same time sufficiently different from 8/3.

The [NiAs] system of intermetallic compounds was the next one to be investigated[15] and the positive and negative results are compared in Table II.

Table I. Superconductivity in the fluorite lattice.

Superconducting	Non-superconducting
$CoSi_2$ (1.3°)	$NiSi_2$; $AuAl_2$; $PtAl_2$

Although NiSb very probably will become superconducting below 1°K, the rest of the negative group becomes either ferromagnetic, antiferromagnetic, or highly paramagnetic a situation which from an empirical point of view excludes superconductivity. Again it is difficult to define a number of valence electrons/atom but it is evident that

$$R > 2$$

in every case where superconductivity was observed.

The column neighboring on Ni, Pd, Pt of the transition elements contains Co, Rh, Ir. Following the above hypothesis concerning R, superconducting rhodium and iridium compounds were discovered. They are Rh_3Ge_2 (structure unknown) at 2.12°K and IrGe (MnP structure) at 4.7°K. The present picture of superconductivity among the transition elements and their compounds in the 8th column is given in Table III.

THE TERNARY SYSTEM OF $(Co,Rh)Si_2$

Any change in the lattice of a superconducting compound of nonsuperconducting elements should give information about the dependence of transition temperature on lattice parameters, as superconductivity is not due to a single dissolved superconducting element but solely to this special crystal lattice.

Table II. Superconductivity in the nickel arsenide lattice.

Superconducting	Non-superconducting
PdSb (1.5°), PtSb (2.1°), PtBi (1.21°)	NiSb, CrSb,[a] MnSb[a]
PdTe (2.3°) (though superconducting PdBi is monoclinic, PtTe does not seem to exist)	NiTe,[b] CoTe

[a] H. Nowotny, Z. Elektrochem. **49**, 254 (1953).
[b] W. Klemm and N. Fratini, Z. anorg. u. allgem. Chem. **251**, 222 (1943)

Our experiments show that if more than two atomic percent of Co in $CoSi_2$ are replaced by one of its neighboring elements such as Fe, Ni, or Rh, the transition temperature drops below 1°K where we were unable to observe. Larger percentages of Fe or Ni did not change this situation. Larger percentages of Rh however began to raise the transition temperature as shown in Fig. 1.

Table III. Superconducting elements and compounds from the 8th column of the periodic system. (The superconducting substances are printed in boldface type.)

Fe	Co	Ni
	$CoSi_2$	**NiBi; $NiBi_3$**
Ru	Rh	Pd
	Rh_3Ge_2	**PdSb; PdBi**
		PdTe; $PdBi_2$
Os	Ir	Pt
	IrGe	**PtSb**
		PtBi

If we suppose that the electronic configuration of Co and Rh are about the same so that the change in mass is the only important factor, then one might have expected the opposite behavior for the transition temperature from Bardeen's and Fröhlich's theories, since Rh is about twice as heavy as Co. Strain could not account for this rise in transition temperature as this would have resulted in a monotonic function. It therefore became evident that the volume had to play a

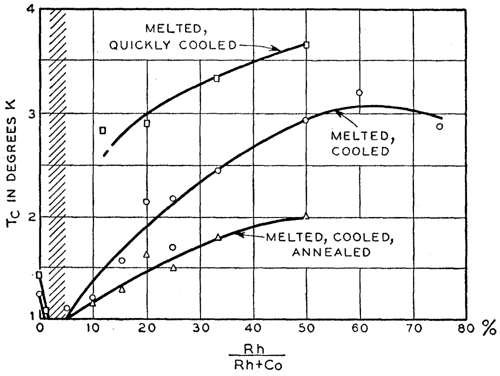

Fig. 1. Transition temperature *vs* percentage of Rh/(Rh+Co) in the melt. (The shaded area indicates no superconductivity above 1°K.)

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[13] B. T. Matthias, Phys. Rev. **89**, 380 (1952).

[14] N. F. Mott and H. Jones, *Properties of Metals and Alloys* (Oxford University Press, London, 1936), pp. 169–170.

[15] B. T. Matthias, Phys. Rev. **90**, 487 (1953).

TABLE IV. Transiton temperature *vs* mass of corresponding elements in the 4th, respectively, 5th column.

Periodic system		M	T_c °K
4. column	Zr	91	0.70
	Hf	179	0.35
5. column	Nb	93	8.3
	Ta	181	4.3

major role, which was different from what Clusius had expected. X-ray investigation by Dr. E. A. Wood has now shown that with mounting Rh percentage there is an initial decrease in molecular volume and an increase thereafter. One can therefore show in this case that a rise in volume partly tends to increase the transition temperature.[16]

THE TERNARY SYSTEM OF Nb(C,N)

This consideration indicated that it might be possible to raise even the transition temperature of superconducting compounds such as NbN at 15.6°K.

The purpose here would be to enlarge the lattice without increasing the total mass nor reducing appreciably the total number of valence electrons/atom. Rögener, in his recent paper on NbN,[17] noticed a similar trend of the change of the transition temperature with the lattice constant. He got a variation of the lattice constant simply by different firing procedures. In our case now we enlarged the lattice by forming solid solutions between NbC−NbN.[18] We observed an increase of the transition temperature to 17.8°K for mixed crystals centering between 25 and 30 atomic percent NbC. This is the highest transition temperature known at this time.

SUPERCONDUCTING ELEMENTS

In the light of these results it may be worthwhile to look at some of the elements again.

With respect to electronic configuration and lattice parameter the pairs Zr−Hf and Nb−Ta are mutually nearly identical. However, their masses and their respective transition temperatures are both different by approximately a factor 2, as shown in Table IV.

The reciprocal linear dependence of the transition temperature upon the mass here is quite different from the isotope effect. Assuming nevertheless that the transition temperatures of the remaining isomorphous elements in the 4th and 5th column, i.e., Ti and V, are determined by this linear dependence of the mass as well as of a change in lattice parameter, one obtains approximately:

$$\frac{d\ln T_c}{d\ln a_0}\approx 13.$$

This exponent 13 is at least in the same order of magnitude as 30, the value deduced by Shoenberg for tin.[19] From Rögener's data on NbN, this value would be about 26. The data for the (Co,Rh)Si_2 system indicate that the lower limit of this exponent would be above 30, if the lattice change were the only decisive factor.

One may therefore conclude that while an increase in mass will lower the transition temperature, an increase in volume will raise it, with an exponent between 4 and 10 for the volume.

The existing superconductors with relatively high transition temperatures indicate that the ***optimum*** ratio of valence electrons/atom seems to be slightly below 5. (See Table V.) While this is at present purely empirical, the closeness of these values to 5 electrons/atom suggests a relation to the half-filled d shell.

TABLE V. Transition temperatures *vs* number of valence electrons/atom.

Element or compound	T_c °K	R = valence electrons/atom
Nb	8–8.3	5[a]
Pb−As	8.4	4.5–5[a]
Pb−Bi	7.3–8.8	≈5[a]
MoC	7.6–8.3	5[a]
ZrN	9.3–9.6	4.5[a]
2 Nb−1 Zr	10.8	4.67[b]
MoN	12–12.5	5.5[a]
V_3Si	17.0	4.75[c]
Nb($C_{0.3}$; $N_{0.7}$)	17.8	4.85[b]

[a] These data are taken from the references in Shoenberg's book (see reference 21).
[b] Indicate present results.
[c] G. F. Hardy and J. K. Hulm, Phys. Rev. **89**, 884 (1953).

My thanks to Professor W. H. Zachariasen, Dr. S. O. Morgan, Dr. J. K. Galt, Dr. H. W. Lewis, and Dr. P. W. Anderson for many helpful discussions and help. I would like to express my gratitude to Dr. E. A. Wood for determining the constants of the mixed crystals, Dr. S. Geller for the structure determination of RhSi, and to Mr. E. Corenzwit for his help with the cryogenics.

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[16] A slight discontinuity at 25 percent was observed, which however was within the accuracy of the measurements.

[17] H. Rögener, Z. Physik **132**, 446 (1952).

[18] P. Duwez and F. Odell, J. Electrochem. Soc. **97**, 299 (1950).

[19] D. Shoenberg, *Superconductivity* (Cambridge University Press, London, 1952).