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Superconductivity

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I. INTRODUCTION

DECENTLY, as a result of the interest in super-K conductivity there has been a renewed effort in the search for superconductors. The possibility of evaluating current theories, particularly the BCS theory, by observing the systematic occurrence or absence of superconductivity has also contributed greatly to the current interest in superconductivity.

Previous review papers and compilations of superconductors have generally been descriptive in nature and presented very few conclusions. In the present paper, we mention some of the conclusions that we have reached as a result of the occurrence of superconductivity and as a result of recent experiments on the isotope effect in transition metals and compounds.

II. MECHANISMS FOR THE OCCURRENCE OF SUPERCONDUCTIVITY

When the occurrence and behavior of superconductors is systematically investigated, they fall naturally into three different groups-the nontransition elements, the transition elements, and intermetallic compounds. Conclusions drawn from the behavior of one group should not be generalized to include the other two without further consideration.

A. Nontransition Elements

Originally it had been assumed that the electronphonon interaction described by the theories of Fröhlich,¹ Bardeen² and later by the modified BCS³

theory was the universal cause of superconductivity. One of the most impressive confirmations for this interaction is the isotope effect, according to which the transition temperatures for different isotopes of the same element vary inversely with the square root of the atomic mass:

$T_{c} \propto 1/\sqrt{M}$

The effect was first observed by Reynolds, Serin, and co-workers⁴⁻⁶ and by Maxwell⁷ for the isotopes of Hg. Since then, the isotope shift has been observed for Zn,⁸ Cd,⁹ Sn,¹⁰⁻¹⁴ Tl,^{15,16} and Pb.^{14,17-19} This was the first direct proof of a lattice-electron interaction as a mechanism for the occurrence of superconductivity.

- Develop. 6, 256 (1962). ⁹ E. Bucher, D. Gross, and J. L. Olsen, Helv. Phys. Acta
- 34, 775 (1961). E. Maxwell, Phys. Rev. 79, 173 (1950); *ibid.* 86, 235 (1952).
- ¹⁰ E. Maxwell, Phys. Rev. 79, 173 (1950); 101a. 30, 253 (1952).
 ¹¹ W. D. Allen, R. H. Dawton, J. M. Lock, A. B. Pippard, and D. Shoenberg, Nature 166, 1071 (1950).
 ¹² W. D. Allen, R. H. Dawton, M. Bär, K. Mendelssohn, and J. L. Olsen, Nature 166, 1071 (1950).
 ¹³ J. M. Lock, A. B. Pippard, and D. Shoenberg, Proc. Cambridge Phil. Soc. 47, 811 (1951).
 ¹⁴ B. Swin, C. A. Bernelda, and C. Lohman, Phys. Rev. 86.

- ⁴ B. Serin, C. A. Reynolds, and C. Lohman, Phys. Rev. 86, 162 (1952).
- E. Maxwell and O. S. Lutes, Jr., Phys. Rev. 86, 649 (1952).
- ¹⁶ N. E. Alekseevskii, Zh. Eksp. i Teoret. Fiz. 24, 240 (1953).
 ¹⁷ M. Olsen, Nature 168, 245 (1951).
 ¹⁸ R. R. Hake, D. E. Mapother, and D. L. Decker, Phys.

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¹ H. Fröhlich, Phys. Rev. **79**, 845 (1950); Proc. Phys. Soc.
(London) A63, 778 (1950).
² J. Bardeen, Phys. Rev. **80**, 567 (1950); *ibid.* **79**, 167 (1950).
³ J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev.

^{108, 1175 (1957);} J. Bardeen and J. R. Schrieffer, "Recent Developments in Superconductivity," Progress in Low Temperature Physics, Vol. III, edited by C. J. Gorter (North-Holland Publishing Co., Amsterdam, 1961), p. 170.
⁴ C. A. Reynolds, B. Serin, W. H. Wright, and L. B. Nesbitt, Phys. Rev. 78, 487 (1950).
⁵ B. Serin, C. A. Reynolds and L. B. Nesbitt, Phys. Rev. 78, 813 (1950).

⁶ C. A. Reynolds, B. Serin, and L. B. Nesbitt, Phys. Rev. 84, 691 (1951).
⁷ E. Maxwell, Phys. Rev. 78, 477 (1950).
⁸ T. H. Geballe and B. T. Matthias, IBM J. Research

Rev. 112, 1522 (1958). ¹⁹ R. W. Shaw, D. E. Mapother, and D. C. Hopkins, Phys. Rev. 121, 86 (1961).

An unnoticed, but important, limitation of the universality of this mechanism was that the isotope effect had been observed only for nontransition elements.

B. Transition Elements

Netzel and Dillinger²⁰ investigated the superconducting transition temperature of the best available Ti isotopes and found that the temperature varied by a factor of 5. As recognized by the authors, the changes in the transition temperature were probably due to other factors, such as the presence of impurities in the samples, rather than to variations in the isotopic mass.

The next transition elements to be studied for an isotope shift were Ru^{21,21a} and Os⁸ whose isotopes are readily available and are inert with respect to carbon, oxygen, and nitrogen at elevated temperatures. The latter is an important consideration, since small amounts of these elements dissolved in the isotope could cause shifts in the transition temperature, which would considerably exceed the shift expected from an isotope effect. No isotope effect at all was observed; the accuracy of the experiments is such that any dependence of the transition temperature upon mass would have to be at least an order of magnitude smaller than for the nontransition elements. The absence of an isotope effect in Ru and in Os seems to indicate that the electron-phonon interaction is not the only mechanism for the occurrence of superconductivity.

Several years ago, when the systematic variation of the transition temperature with the number of valence electrons was discovered for the transition elements and compounds, it became clear that there was another mechanism for the occurrence of superconductivity. High transition temperatures always coincided with an odd number of electrons, thus indicating the influence of a net spin and, consequently, a magnetic interaction. This will be discussed later in the paper.

Recent experiments, in which the transition temperature of Ti and of Zr were raised by the addition of magnetic impurities only, point to a spin-exchange interaction mechanism for superconductivity. The experiments of Andres, Olsen, and Rohrer,²² which show a change in sign for the interaction constant vs volume dependence in going from nontransition elements to transition elements, also indicate the existence of this mechanism. Further evidence that the phonon mechanism is not applicable comes from a consideration of the relationship between the heat capacities and transition temperatures of superconductors in the 3rd, 8th, and 9th columns of the periodic table. For these elements, the transition temperature varies inversely with the electronic heat capacity which is contrary to the behavior expected from the BCS theory.²³ The recent discovery that superconductivity in Mo is suppressed by the presence of few parts per million of Fe may be another indication of this mechanism.

C. Intermetallic Compounds

The results of the isotope effect experiments in intermetallic compounds point to a combination of the two mechanisms mentioned above or possibly to a third mechanism for the occurrence of superconductivity. Devlin and Corenzwit²⁴ examined the variation of the superconducting transition temperatures of Nb₃Sn, containing different isotopes of Sn, and found that the effect was almost an order of magnitude less than the calculated value based on the $1/\sqrt{M}$ relationship. It was not obvious whether these results obtained by varying the Sn mass were significant, since it could be argued that the superconducting wave functions were associated primarily with the Nb. Therefore, an investigation of the isotope effect in the compound Mo₃Ir was undertaken substituting the various isotopes of Mo.²⁵ In this way the mass was varied at the sites, where the superconducting wave functions should be at a maximum. The effect observed is intermediate between that of the nontransition elements and that of the Ru and Os. Strangely enough, the isotope effect in the element Mo has the same value namely, $T_{a} \propto M^{-1/3}$. It seems reasonable, therefore, to assume that there is a mechanism causing superconductivity in compounds and in Mo, which may be intermediate between the electron-phonon interaction for nontransition elements and the spin-exchange mechanism for Ru and Os.

²⁰ R. G. Netzel and J. R. Dillinger, "Superconducting Tran-Proceedings of the VIIth International Conference on Low Temperature Physics, edited by G. M. Graham and A. C. Hollis Hallett (University of Toronto Press, Canada, 1961),

p. 389. ²¹ T. H. Geballe, B. T. Matthias, G. W. Hull, Jr., and E. Corenzwit, Phys. Rev. Letters 6, 275 (1961).

^{21a} Note added in proof. D. K. Finemore and D. E. Mapother [Phys. Rev. Letters 9, 288 (1962)] confirm the absence of an isotope effect in superconducting Ru.

 ²² K. Andres, J. L. Olsen, and H. Rohrer, IBM J. Research Develop. 6, 84 (1962).
 ²³ D. Pines, Phys. Rev. 109, 280 (1958).

²⁴G. E. Devlin and E. Corenzwit, Phys. Rev. 120, 1964 (1960).²⁵ B. T. Matthias, T. H. Geballe, E. Corenzwit, and G. W.

Hull, Jr., Phys. Rev. (to be published).

III. OCCURRENCE OF SUPERCONDUCTIVITY

A. Empirical Rules

While it does not seem possible at present to encompass all superconductors with a unified description or theory, it has been possible to establish empirically the necessary conditions for the occurrence of superconductivity and a criterion for the transition temperatures.26,27

If N is defined as the number of valence electrons per atom, counting as such all the electrons outside of a filled shell, then superconductivity is found only when N is appreciably greater than 1 or less than 10^{28} Almost all the superconductors known to date follow this rule. In the superconducting range the transition temperature is usually an oscillatory function of N. This applies only to the transition elements. N can be changed continuously by forming solid solutions or intermediate phases of elements within the same group. In contrast to this, solid solutions of nontransition elements in transition elements or vice versa destroy superconductivity rather rapidly. This again is a clear indication of the difference in mechanisms leading to superconductivity.

B. Elements

Elements which have less than two or more than nine valence electrons per atom are not superconducting at the lowest temperatures measured to date. Elements with two valence electrons are borderline cases. The transition temperatures of the transition elements may be represented by an oscillatory function of N:

$$T_{\rm c} \propto V^{x} f(N)$$

where T_{e} varies for the different crystal systems, for the atomic volume, and for the atomic mass. The limitations of this formulation have been discussed previously.26

The transition temperatures of the elements have been reviewed by Shoenberg,²⁹ by Eisenstein,³⁰ and by Roberts.³¹ Recently, Goodman³² discussed the possible

²⁹ D. Shoenberg, Superconductivity, (Cambridge University Press, Cambridge, 1960), p. 222.
³⁰ J. Eisenstein, Rev. Mod. Phys. 26, 277 (1954).
³¹ B. W. Roberts, "Superconducting Materials and Some of Their Properties," General Electric Co. Rept. No. 61-RL-2744M, June, 1961.
³² B. B. Goodman, Compt. Rend. 250, 683 (1960).

existence of superconducting elements with extremely low transition temperatures.

The transition temperatures of the superconducting elements arranged according to crystal-structure types are given in Table I (references 33 to 78). The

³³ G. Seidel and P. H. Keesom, Phys. Rev. 112, 1083 (1958). ³⁴ J. F. Cochran and D. E. Mapother, Phys. Rev. 111, 132 (1958)

³⁵ N. E. Phillips, "Heat Capacity of Copper and Aluminum between 0.3° and 4.2°K," Proceedings of the Fifth Inter-national Conference on Low Temperature Physics and Chemistry, edited by J. R. Dillinger (University of Wisconsin Press, Madison, Wisconsin, 1958), p. 414.

³⁶ D. L. Martin, Proc. Phys. Soc. (London) 78, 1489 (1961).
 ³⁷ W. B. Pearson, A Handbook of Lattice Spacings and Structures of Metals and Alloys (Pergamon Press, New York, 1958).
 ³⁸ W. T. Ziegler, R. A. Young, and A. L. Floyd, Jr., J. Am. Chem. Soc. 75, 1215 (1953).
 ³⁹ A. Barmon, M. W. Zurnersky, and M. A. B. Karn, Distance and M. M. Struck, and M. K. Struck, and M. Struck, and M.

- ³⁹ A. Berman, M. W. Zemansky, and H. A. Boorse, Phys. Rev. **109**, 70 (1958).
- ⁴⁰ G. S. Anderson, S. Legvold, and F. H. Spedding, Phys. Rev. **109**, 243 (1958).

⁴¹ K.A. Gschneidner, Jr. and B. T. Matthias, "Electrical and Magnetic Properties of the Rare Earth Metals, Their Alloys and Compounds," *Rare Earth Research*, edited by E. V. Kleber (The Macmillan Co., New York, 1961), p. 158.
⁴² R. A. Hein, J. W. Gibson, B. T. Matthias, T. H. Geballe, and E. Corenzwit, Phys. Rev. Letters 8, 408 (1962).
⁴³ W. B. Paerera and L. M. Tampleton, Phys. Rev. 100

⁴³ W. B. Pearson and I. M. Templeton, Phys. Rev. 109,

1094 (1958). ⁴⁴ J. P. Franck and D. L. Martin, Can. J. Phys. **39**, 1320 ⁴⁴ J. P. Franck and D. L. Martin, Can. J. Phys. 39, 1320 (1961).
 ⁴⁵ D. Schoenberg, Proc. Cambridge Phil. Soc. 36, 84 (1940).
 ⁴⁶ N. M. Wolcott and R. A. Hein, Phil. Mag. 3, 591 (1958).
 ⁴⁷ A. Wexler and W. S. Corak, Phys. Rev. 85, 85 (1952).
 ⁴⁸ H. A. Boorse, A. T. Hirshfield, and H. Leupold, Phys. Rev. Letters 5, 246 (1960).
 ⁴⁰ W. D. G. F. N. L. D. R. Am. Phys. Gap. 6

⁴⁹ W. DeSorbo and G. E. Nichols, Bull. Am. Phys. Soc. 6, 267(1961).

T. H. Geballe, B. T. Matthias, E. Corenzwit, and G. W. Hull, Jr., Phys. Rev. Letters 8, 313 (1962). ⁵¹ J. I. Budnik, Phys. Rev. 119, 1578 (1960). ⁵² R. W. Shaw, D. E. Mapother, and D. C. Hopkins, Phys.

Rev. 120, 88 (1960).

⁵³ C. A. Swenson and C. H. Hinrichs, "The Pressure Effect in Superconducting Tantalum," *Proceedings of the VIIth In-ternational Conference on Low Temperature Physics*, edited by C. M. Craham and A. C. Hallist, *University* (2019) G. M. Graham and A. C. Hollis Hallett (University of Toronto

 ⁵⁴ J. G. C. Milne, Phys. Rev. 122, 387 (1961).
 ⁵⁵ T. S. Smith, W. B. Gager, and J. G. Daunt, Phys. Rev. 89, 654 (1953).

M. C. Steele and R. A. Hein, Phys. Rev. 92, 243 (1953).
 T. S. Smith and J. G. Daunt, Phys. Rev. 88, 1172 (1952).

⁵⁸ J. F. Cochran and D. E. Mapother, Phys. Rev. 121, 1688 (1961). ⁵⁹ N. E. Phillips, Phys. Rev. Letters 1, 363 (1958) E. Coronzwit, J. P. Maita, B. T. J

⁶⁰ N. E. Finings, Fhys. Rev. Letters 1, 605 (1969).
 ⁶⁰ V. B. Compton, E. Corenzwit, J. P. Maita, B. T. Matthias, and F. J. Morin, Phys. Rev. 123, 1567 (1961).
 ⁶¹ J. G. Daunt and J. W. Cobble, Phys. Rev. 92, 507 (1953).
 ⁶² B. B. Goodman, Nature 167, 111 (1951).
 ⁶³ J. K. Hulm and B. B. Goodman, Phys. Rev. 106, 659 (1977).

(1957)⁶⁴ J. A. Carruthers and A. Connolly, "Some Superconductors below 1°K," Proceedings of the Fifth International Conference on Low Temperature Physics and Chemistry," edited by J. R. Dillinger (University of Wisconsin Press, Madison, Wisconsin,

 ⁶⁵ R. Blanpain, Bull. Classe Sci. Acad. Roy. Belg. 47, 750 (1961).

 ⁶³ E. Maxwell and O. S. Lutes, Phys. Rev. 95, 333 (1954).
 ⁶⁹ C. A. Bryant and P. H. Keesom, Phys. Rev. 123, 491 (1961).

²⁶ B. T. Matthias, "Superconductivity in the Periodic System," *Progress in Low-Temperature Physics*, Vol. II, edited by C. J. Gorter (North-Holland Publishing Co., Amsterdam,

²⁷ B. T. Matthias, Phys. Rev. **97**, 74 (1955). ²⁸ The earlier formulation of this rule, which stated that superconductivity above 1°K occurs only for $2 \le N \le 8$ is essentially correct but must be extended somewhat when temperatures below 1°K are considered.

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	Superconducti	ivity data		Сгу	vstal-structu	ıre data		
Element	Transition temperature ^a °K	References	Structure type	System	Lattice a, Å	Constants b, Å	с, Ă	References
A1	1.171-1.196	33, 34, 35, 36	A1–Cu	Cubic	4.0496			37
β -La	5.4-6.3	35, 50 38, 39, 40, 41, c	A1–Cu	Cubic	5.296			38
Ir Pb	0.14 7.175-7. <i>193-</i> 7.23	$42 \\ 33, 43, 44$	A1–Cu A1–Cu	Cubic Cubic	$3.8389 \\ 4.9502$			37 37
α -Th	1.37	45, 46	A1–Cu	Cubic	5.0843			37
VNb	5.03- $5.139.09$ - 9.465	$33, 47 \\ 33, 48, 48,$	A2– WA 2– W	Cubie Cubie	$3.0282 \\ 3.3007$			$37 \\ 37$
Mo Ta	0.92 4.39-4.482	$ \begin{array}{r} 49 \\ 25, 50 \\ 33, 51, \\ 52, 53, \end{array} $	A2-W A2-W	Cubic Cubic	$3.1468 \\ 3.298$			37 37
		54			3.8389			
Ti	0.387- 0.49	55, 56,	A3–Mg	Hexagonal	2.9504		4.6833	37
Zn	0.825-0.855-0.875	57 8, 33, 58, 59	<i>A3</i> –Mg	Hexagonal	2.6649		4.9468	37
Zr Tc Ru	0.546-0.565 8.22-9.3-11.2 0.47-0.493	57 60, 61, b 21, 62, 63 64	$egin{array}{c} A3-{ m Mg}\ A3-{ m Mg}\ A3-{ m Mg}\ A3-{ m Mg} \end{array}$	Hexagonal Hexagonal Hexagonal	$3.2312 \\ 2.735 \\ 2.7058$		$5.1477 \\ 4.388 \\ 4.2816$	37 37 37
Cd	0.52-0.602	33, 57, 65	A3-Mg	Hexagonal	2.9788		5.6167	37
$_{ m Re}^{ m Hf}$	$0.165 \\ 1.699$ - 2.42	78 63, 66, 67	$egin{array}{c} A{\it 3} extrm{-Mg}\ A{\it 3} extrm{-Mg} \end{array}$	Hexagonal Hexagonal	$\begin{array}{c} 3.1946 \\ 2.760 \end{array}$		$\begin{array}{c} 5.0511 \\ 4.458 \end{array}$	37 37
Os	0.58 - 0.655 - 0.71	8, 62, 63, 64	<i>A3</i> –Mg	Hexagonal	2.7353		4.3191	37
\mathbf{Tl}	2.36 - 2.39	33, 68	A3–Mg	Hexagonal	3.4566		5.5248	37
α -La	4.8 - 4.9 - 5.0	39, 40,	A3'–La	Hexagonal	3.770		12.159	37
Sn	3.701-3.722	41, c 33, 52, 69	A5–White Sn	Tetragonal	5.8314		3.1814	37
In	3.396-3.408	33, 52, 70, 71	A6-In	Tetragonal	4.5979		4.9467	37
α -Hg	4.153		<i>A10</i> –Hg	Rhombohedral	2.9863	$\alpha=70^\circ\!44.6^\prime$		37
Ga α-U β-Hg	1.087-1.103 0.68-0.7 3.949	33, 58 74, 75 72, 73	<i>A11</i> –Ga <i>A20–</i> α–U	Orthorhombic Orthorhombic Tetragonal	$\begin{array}{c} 4.5198 \\ 2.8536 \\ 3.995 \end{array}$	$7.6602 \\ 5.8698$	$\begin{array}{c} 4.5258 \\ 4.9555 \\ 2.825 \end{array}$	37 76 77

TABLE I. Transition temperatures and crystal-structure data of superconducting elements.

^a In our opinion the italic values of *Tc* appear to be the most reliable. ^b Note added in proof. M. L. Picklesimer and S. T. Sekula [Phys. Rev. Letters 9, 254 (1962).] recently reported the transition temperature of 99.995% To as 8.22°K. ^c Note added in proof. K. Schwidtal, Z. Physik 169, 564 (1962).

occurrence of superconductivity seems to be most favorable in structure types A1, A2 and A3.

A1-Cu type, face-centered cubic

The fact that Mo became superconducting after purification in an arc furnace^{25,50} prompted an investigation of the superconducting properties of Ir treated in a similar manner. Pure Ir is superconducting at the relatively low temperature of 0.14°K,⁴² and this indicates that superconducting transition temperatures cannot be predicted from the value of the electronic specific heat. For example, the electronic specific heat⁷⁹ γ of Ir is 3.1 mj/mole-deg,² and the transition

 ⁷⁰ H. Meissner and R. Zdanis, Phys. Rev. 109, 681 (1958).
 ⁷¹ M. D. Reeber, Phys. Rev. 117, 1476 (1960).
 ⁷² J. E. Schirber and C. A. Swenson, Phys. Rev. 123, 1115

⁷² J. E. Schirber and C. A. Swenson, FHys. Rev. 120, 1110 (1961).
⁷³ C. A. Swenson and J. E. Schirber, "Superconducting Properties of the Two Modifications of Mercury," Proceedings of the VIIth International Conference on Low Temperature Physics, edited by G. M. Graham and A. C. Hollis Hallett (University of Toronto Press, Canada, 1961), p. 338.
⁷⁴ R. A. Hein, W. E. Henry, and N. M. Wolcott, Phys. Rev. 107, 1517 (1957).
⁷⁵ T. G. Berlincourt, "Size Effect in the Hall Coefficient of Cu, and Superconductivity of Metastable U-Base Mo Alloys," Proceedings of the Fifth International Conference on Low Temp.

Proceedings of the Fifth International Conference on Low Tem-(University of Wisconsin Press, Madison, Wisconsin, 1958),

⁽University of A.S.Cooper, Acta Cryst. 15, 578 (1962).
⁷⁶ A. S. Cooper, Acta Cryst. 15, 578 (1962).
⁷⁷ M. Atoji, J. E. Schirber, and C. A. Swenson, J. Chem.
Phys. 31, 1628 (1959).
⁷⁸ R. A. Hein (private communication.)

⁷⁹ N. M. Wolcott, "The Specific Heat of Transition Metals,"

temperature⁴² is 0.14°K; for Os γ is 2.35,⁷⁹ and the transition temperature⁸ is 0.655° K; and for Mo γ is 1.91,⁸⁰ and the transition temperature is 0.92°K.^{25,50}

The superconducting properties of the two forms of La indicate that the cubic close-packed structure is more favorable for the occurrence of superconductivity than the hexagonal close-packed structure. The face-centered cubic form of La has a transition temperature of 6.3°K, whereas that of the hexagonal close-packed form is 4.9°K.⁴¹ Results of an investigation of superconductivity in Os-Ir solid solutions also show that for the same valence-electron concentration the cubic close-packed structure is more favorable than the hexagonal close-packed structure.⁸¹ In both structures, however, the transition temperature is proportional to $1/\gamma$.

The following elements have been investigated for superconductivity and have been found normal at the temperatures given: α-Ca-0.35°K,⁸² Co-1.36°K,⁸³ Ni-0.35°K,⁸² Cu-0.05°K,⁸³ α-Sr-0.35°K,⁸² Rh-0.086° K,⁸⁵ Pd-0.10°K,⁶² Ag-0.35°K,⁸² Ce-0.25°K,⁶² Yb-0.35°K,82 Pt-0.10°K,62 and Au-0.05°K.83

A2-W type, body-centered cubic

Most of the nonferromagnetic elements with this structure and with a favorable number of valence electrons are superconducting. Cr, Mo, and W each with six valence electrons are located in a minimum in a plot of the number of valence electrons vs. transition temperature.²⁷ The superconducting properties of very dilute solutions of Re in Mo suggested that pure Mo would be superconducting and in fact, pure Mo becomes superconducting at about 0.92°K.^{25,50} Wolfram can become superconducting if its N is slightly changed; for example a few percent of Rh²⁷ or of Pt⁸¹ dissolved in it will render the metal superconducting. However, strictly speaking, the superconducting property is associated with the solid solution and not with the element.

The following elements have been investigated for superconductivity and have been found normal at the temperatures given: Na-0.09°K,62 K-0.08°K,62 Cr0.082°K,⁸⁵ Fe-0.75°K,⁸⁴ Rb-0.8°K,⁸⁶ Cs-0.35°K,⁸² Ba-0.15°K,62 and W-0.035°K.87

A3-Mq type, close-packed hexagonal

This structure is particularly favorable for the occurrence of superconductivity among the transition elements with N < 6. Technetium (N = 7) has the highest known transition temperature for an element, namely 11.2°K.^{61,87a} For N < 6, Ti, Zr and Hf are superconductors. Recently, Hein⁷⁸ has determined that various samples of highly purified Hf become superconducting at 0.165°K.

These elements have been investigated for superconductivity and have been found normal at the temperatures given: Li-0.08°K,⁶² Be-0.064°K,⁸⁵ Mg-0.05°K,⁸³ Sc-0.08°K,⁶⁴ Co-1.36°K,⁸³ Y-0.07°K,⁸⁷ Er-0.8°K,86 Tm-0.35°K,82 and Lu-0.35°K.82

The occurrence of superconductivity in the elements with A3'-, A4-, A7-, A8- and A12-type structures has been investigated. Alpha-Pr and α -Nd which crystallize in the hexagonal La-type structure (A3') are not superconducting above 0.25°K.62 The semiconducting elements Si, Ge, and Sn (grey) have the diamond-type A4 structure and are not superconducting above 0.073,85 0.05,83 and 1.32°K,88 respectively. For the semimetals the rhombohedral Astype structure (A7) seems to be unfavorable for the occurrence of superconductivity. Arsenic is normal down to 0.8°K,86 Sb to 0.152°K85 and Bi to 0.05°K.83 Selenium and Te have the trigonal Se-type structure (A8) and are normal above 1.26°K.⁸⁹ Although cubic α -Mn (A12-type structure) is not superconducting above 0.15°K,⁶² this structure is a favorable one for the occurrence of superconductivity in transition metal compounds. This is the first example of superconductivity occurring in a structure which lacks a center of symmetry.

The absence of superconductivity in many of the elements investigated may be due to the presence of extremely small amounts of impurities as illustrated by the behavior of Mo. For this reason it is important that further investigations work in the direction of higher purity as well as lower temperatures.

Several elements occur in two modifications, one of which is superconducting. The first one to be dis-

Conférence de Physique des Basses Températures (Centre de la Recherche Scientifique and UNESCO, Paris, 1956), p. 286. ⁸⁰ C. A. Bryant and P. H. Keesom, J. Chem. Phys. **35**, 1149 (1961).

 ⁽¹³⁾ T. H. Geballe, B. T. Matthias, V. B. Compton, E. Corenzwit, and G. W. Hull, Jr., Phys. Rev. (to be published).
 ⁸² Results of present investigation.

⁸³ N. Kürti and F. Simon, Proc. Roy. Soc. (London) A151, 610 (1935).

⁸⁴ W. H. Keesom, Commun. Kamerlingh Onnes Lab. Univ. Leiden 21, No. 230, 1 (1934). ⁸⁵ N. E. Alekseevskii and L. Migunov, J. Phys. (U.S.S.R.)

^{11, 95 (1947).}

⁸⁶ E. Justi, Neue Phys. Blätter 8, 207 (1946); data quoted in reference 29.

⁸⁷ M. Strongin and H. A. Fairbank, "A Search for New Superconductors," Proceedings of VIIth International Con-ference on Low Temperature Physics, edited by G. M. Graham and A. C. Hollis Hallett (University of Toronto Press, Canada, 1961), p. 377.

^{87a} Note added in proof. The transition temperature has recently been determined as 8.22°K (see Table I). ⁸⁸ G. Sharvin, J. Phys. (U.S.S.R.) 9, 350 (1945). ⁸⁹ W. Meissner and B. Voigt, Ann. Phys. 7, 892 (1930).

covered was tin. Grev tin, which has the cubic A4diamond-type structure is a semiconductor and does not become superconducting above 1.32°K88; whereas white tin with a tetragonal A5-type structure is a superconductor. Beryllium and Bi, which are normally nonsuperconductors, become superconducting when condensed as thin films at about 4°K. The transition temperature for Be in this form is 8.0°K,^{90,91} and for Bi, 6.0°K.^{92,93} It is possible that Mg and Sc might show similar behavior. The transition temperature of thin films of Ga condensed at about 4°K is 8.4°K^{94,95} compared with 1.09°K for the usual form of Ga. Two high-pressure superconducting modifications of Bi have been observed. One formed at 25 000 atm has a transition temperature of 3.93°K and the other formed at 25 000 to 29 000 atm has a transition temperature of 7.25°K.⁹⁶

C. Alloys

1. Solid Solutions

Nontransition elements. Representative examples of complete solid solutions between nontransition elements are somewhat limited by the lack of any extended solid solubility between them. For this reason it has not been possible to follow the relationship between the valence-electron concentration and the transition temperature through any maxima or minima, if present, without a change in crystal structure. However, in the systems investigated to date, the transition temperature never changes appreciably with composition.

Superconductivity in the Hg–In system has been investigated by Reeber⁷¹ and by Merriam and Jensen.⁹⁷ Reeber restricted the study to solid solutions containing up to 7 at. % In and found that the transition temperature did not vary appreciably with composition. Merriam and Jensen studied superconductivity in the system up to 85 at. % In. The tran-

sition temperature ranged from less than 3.2°K for a 20 at. % In alloy to 4.5°K for a 80 at. % In alloy. However, the solid-solution range is not appreciable, and the relative insensitivity of the transition temperature to changes in crystal structure seems remarkable.

Stout and Guttman⁹⁸ have investigated the superconducting properties of solid solutions containing up to 50 at. % Tl in the In–Tl system. The transition temperature decreases with increasing amounts of Tl and the transition temperature of the 50 at. % alloy is 2.652°K. The transition temperatures of solid solutions in the Sn–Sb and in the Sn–Bi systems have been studied in the composition range 0 to 8 at. % Sb and 0 to 10 at. % Bi.99 In both systems the transition temperature increases with increasing values of Nand for an alloy containing 10 at. % Bi the transition temperature is 4.18°K.

Shoenberg¹⁰⁰ has summarized much of the data for solid solutions of nontransition elements.

Transition elements. The superconducting properties of solid solutions of transition elements have received considerable attention which is due to the very extensive range of solid solutions formed between these elements. In addition, the transition temperatures of these solid solutions changes appreciably with variations in the valence-electron concentration which is in marked contrast to the effect in nontransition element solid solutions.

Hulm and Blaugher¹⁰¹ have investigated the superconducting solid solutions of the transition elements. Plots of transition temperature vs composition are given for binary alloys of neighboring elements in a row, for binary alloys of diagonal neighbors, and for alloys of neighbors in columns.

The transition temperature of all superconducting elements may be raised or lowered by solid-solution formation in accordance with the described empirical rules. The transition temperature of Ti is raised by the addition of any transition element to the right of it in the periodic table. Solid solutions of Ti with V, 101, 102 Zr, 101 Nb, 101, 102 and Mo103, 104 have been investigated. The depression of the transition tempera-

⁹⁰ B. G. Lazarev, A. I. Sudovtsev, and A. P. Smirnov, Soviet Phys.—JETP 6, 816 (1958).
⁹¹ B. G. Lazarev, A. I. Sudovtsev, and E. E. Semenenko, Soviet Phys.—JETP 10, 1035 (1960).
⁹² R. Hilsch, "Superconductive Properties of Metal Layers," Proceedings of the International Conference on Low Tempera-ture Physics, edited by R. Bowers (Oxford, 1951), p. 119.
⁹³ N. V. Zavaritskii, Doklady Akad. Nauk S.S.S.R. 86, 687 (1952)

^{(1952).} ⁹⁴ W. Buckel and R. Hilsch, Z. Physik **138**, 109 (1954). "Concernductivity and Free Electron."

⁹⁵ W. Buckel, "Superconductivity and Free Electron Con-centration of Condensed Bismuth and Gallium Films," Proceedings of the Fifth International Conference on Low Tempera-ture Physics and Chemistry, edited by J. R. Dillinger (Univer-sity of Wisconsin Press, Madison, Wisconsin, 1958), p. 326. ⁹⁶ N. B. Brandt and N. I. Ginzberg, Soviet Phys.—JETP 12, 1009 (1961)

 ¹¹ 12, 1082 (1961).
 ⁹⁷ M. F. Merriam and M. A. Jensen, Bull. Am. Phys. Soc. 7, 176 (1962); Private communication.

 ⁹⁸ J. W. Stout and L. Guttman, Phys. Rev. 88, 703 (1952).
 ⁹⁹ W. F. Love, Phys. Rev. 92, 238 (1953).
 ¹⁰⁰ D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1960), p. 230.
 ¹⁰¹ J. K. Hulm and R. D. Blaugher, Phys. Rev. 123, 1569

^{(1961).} ¹⁰² E. Bucher and J. Müller, Helv. Phys. Acta **34**, 410 (1961). ¹⁰³ R. R. Hake, D. H. Leslie, and T. G. Berlincourt, J. Phys.

Chem. Solids 20, 177 (1961). ¹⁰⁴ R. D. Blaugher, B. S. Chandrasekhar, J. K. Hulm, E. Corenzwit, and B. T. Matthias, J. Phys. Chem. Solids 21, 252 (1961).

ture of V by solid-solution formation with Cr,¹⁰⁵ Mn,¹⁰⁵ Fe,¹⁰⁵ Co,¹⁰⁵ Ni,¹⁰⁵ Nb,¹⁰¹ and Mo¹⁰⁶ is also due to changes in the valence-electron concentration. The addition of almost every transition element to the right of Zr in the periodic table will increase its transition temperature. This has been observed in solid solutions of Zr with Ru,107 Rh,27 Pd,107 Os,107 Ir,107 Pt,¹⁰⁷ and even with Au¹⁰⁷ which is a borderline element. The largest increase in the transition temperature occurs in a Zr alloy containing 15 at. % Rh which has a transition temperature of about 9°K.

The transition temperature of Nb is increased by additions of Ti,¹⁰¹ Zr,^{101,108} or Hf.¹⁰¹ In Nb-Zr solid solutions the maximum transition temperature occurs near 11°K for an alloy containing 20 to 30 at. %Zr.¹⁰⁸ The transition temperature of Nb is lowered by solid-solution formation with any transition element to the right of it in the periodic table. This effect has been reported for solid solutions of Nb with Cr,¹⁰¹ Mo,101,109,110 Ta,101 and W.101

The variation of transition temperature with composition for Nb-Mo solid solutions has been investigated to temperatures below 0.25°K. Blaugher and Hulm¹⁰¹ describe the superconducting behavior down to 1°K; Hulm, Blaugher, Geballe, and Matthias¹⁰⁹ for the temperature range 0.3 to 1.0°K; Hein and co-workers¹¹⁰ for temperatures below 0.25°K. The depression of the transition temperature for solid solutions containing up to about 42 at. % Mo is roughly proportional to the concentration. The transition temperature vs composition data for alloys containing more than 42 at. % Mo (temperatures below 0.25°K) seemed to indicate that the transition temperature vs composition curve was no longer linear and suggested that the temperature was approaching zero in an asymptotic manner. However, we do not believe that this is valid, since the deviation from linearity begins only at temperatures of the order of the width of the transition itself ($< 0.1^{\circ}$ K). Inhomogeneities or any deviation from a perfect solid solution would give such an effect. In addition, the effect of magnetic impurities will be appreciable in this temperature range and therefore, the present data should be considered with some caution.

The transition temperature of Mo is raised when

any of the elements listed below are dissolved in it:

$$\frac{\text{Tc}}{\text{Re}} \quad \frac{\text{Ru}}{\text{Os}} \quad \text{Rh} \quad \text{Pd}$$

The underlined elements are superconducting. The variation of the transition temperature with composition and therefore with N has been studied for the solid solutions Mo-Tc,60 Mo-Ru,27,111 Mo-Rh,112 and Mo-Re.¹¹³ Rather high transition temperatures have been observed for Mo-Re solid solutions; the maximum transition temperature is somewhat above 12°K for an alloy containing 40 at. % Re. In solid solutions of Mo and Rh, in which the maximum solubility is 16 at. % Rh, the transition temperature is 8°K for this concentration.

The transition temperatures of solid solutions of Ru containing 50 at. % Mo or W have been reported as 9.5 to 10.5 and 7.5°K, respectively.²⁷

Anderson, Legvold, and Spedding⁴⁰ studied the superconducting properties of solid solutions in the La-Y and in the La-Lu systems. In both systems the transition temperature decreases with decreasing amounts of La in the alloys.

Blaugher, Taylor, and Hulm¹¹³ report that the β -Hf region in both the Mo-Hf and Re-Hf systems is superconducting. For Mo–Hf alloys the maximum transition temperature is 2.5°K and in the Re-Hf system an alloy containing 87.5 at. % Hf has a transition temperature of 1.70°K. The variation in the valenceelectron concentration accounts for the increase in the transition temperature of Ta by the addition of Hf¹⁰¹ and for its decrease by the addition of W.¹⁰¹

It has been possible to induce superconductivity in an element which is normal in the observable temperature range by the formation of a solid solution. For example, W which is normal down to 0.035°K⁸⁷ becomes superconducting when a few percent Pt is dissolved in it.⁸¹ Similarly 30 at. % of W dissolved in Pt will render this element superconducting at 0.40°K. The same elements which raise the transition temperature of Mo should also form superconducting solid solutions with W. The transition temperatures of solid solutions of W-Re,113 W-Os,113 and W-Pt81 have been investigated as a function of composition. The transition temperature of a W solid solution containing 25 at. % Re is about 4.6° K; for a 10 at. % Os

¹⁰⁵ J. Müller, Helv. Phys. Acta 32, 141 (1959)

¹⁰⁶ E. Bucher, G. Busch and J. Müller, Helv. Phys. Acta 32,

^{318 (1959).} ¹⁰⁷ B. T. Matthias and E. Corenzwit, Phys. Rev. 100, 626

 <sup>(1955).
 &</sup>lt;sup>108</sup> B. T. Matthias, Phys. Rev. 92, 874 (1953).
 ¹⁰⁹ J. K. Hulm, R. D. Blaugher, T. H. Geballe, and B. T. Matthias, Phys. Rev. Letters 7, 302 (1961).
 ¹¹⁰ R. A. Hein, J. W. Gibson, and R. D. Blaugher, Bull. Am.

Phys. Soc. 7, 322 (1962).

¹¹¹ B. T. Matthias, T. H. Geballe, V. B. Compton, E. Corenzwit, and G. W. Hull, Jr., Phys. Rev. (to be published).
¹¹² B. T. Matthias, E. A. Wood, E. Corenzwit, and V. B. Bala, J. Phys. Chem. Solids 1, 188 (1956).
¹¹³ R. D. Blaugher, A. Taylor, and J. K. Hulm, IBM J. Research Develop. 6, 116 (1962).

solid solution it is about 1.5° K; and for 5 at. % Pt it is about 2.2°K.

Solid solutions of V in Re raise the transition temperature of Re rather sharply. For an alloy containing 10 at. % V the transition temperature is 9.4°K.⁸² Solid solutions of Hf in Re also show this very remarkable behavior and for a Re solid solution containing 2.5 at. % Hf the transition temperature is 7.3°K.¹¹³ The superconducting properties of Os-Ir solid solutions have been described earlier in the paper.

The superconducting properties of Th-Y solid solutions in the composition range of 0-55 at. % Y have been investigated.⁴¹ There is a maximum in the transition temperature at 1.76°K for an alloy containing 25 at. % Y. At the present time, it is not clear whether this maximum is due to the variation in electron concentration or to the onset of a depression in the transition temperature by a magnetic interaction introduced by Y.

The variation of the transition temperature with composition has been investigated for U-Mo and U-Nb solid solutions.¹¹⁴⁻¹¹⁶ Chandrasekhar and Hulm¹¹⁴ obtained a hypothetical transition temperature of 1.8°K for γ -body-centered cubic U by extrapolating their U-Nb solid solution data. An extrapolation of the data in the orthorhombic α -U region yields a transition temperature of 0.7° K for α -U which agrees reasonably well with the measured value of 0.68°K.74

Solid solutions of the ferromagnetic and of the antiferromagnetic elements in Ti,¹¹⁷ and also to some extent in Zr,¹⁰⁷ raise the transition temperature of Ti and of Zr, respectively. The increase in the transition temperature of Ti by adding small amounts of Cr. Mn, Fe, or Co is larger than that expected solely from a change in the valence-electron concentration. This is seen by comparing the transition temperatures of solid solutions of Ti with elements having a magnetic moment with those of the corresponding solid solutions containing nonmagnetic elements but having the same valence; for example, Ti–Fe vs. Ti–Ru or Ti-Co vs Ti-Rh. The transition temperature vs composition curve for Ti-Fe and for Ti-Ru solid solutions is given in Fig. 1. This is also illustrated by the effect of identical amounts of Fe and of Ru on the transition temperature of a Ti_{0.60} V_{0.40} alloy.¹¹⁸ The temperature is lowered much less for additions of Fe than for Ru. Therefore, it would seem that the super-



FIG. 1. Superconducting transition temperatures of Fe or Ru solid solutions in Ti.¹¹⁷

conductivity of dilute Ti and Zr solid solutions with the magnetic elements is enhanced by some kind of a magnetic interaction.

On the other hand, the transition temperature of a $M_{0.80}$ Re_{0.20} solid solution is lowered drastically by the addition of small amounts of metals belonging to the first row of the transition series.¹¹⁹ For example, the temperature decreases linearly with the concentration of Fe at a rate of 22° per at. % Fe. This lowering of the transition temperature of $Mo_{0.80}$ Re_{0.20} by a 3d element is due to a localized magnetic moment and is analogous to the effects produced by the magnetic rare-earth ions in La, which will be described later in the paper. The addition of small amounts of Fe to Nb-Mo solid solutions (containing up to 40 at. %Mo) does not, however, result in any appreciable reduction in the transition temperature indicating that Fe does not exhibit a localized moment in these alloys. However, as the amount of Mo is increased a localized moment appears. Clogston and co-workers¹²⁰ have investigated the occurrence of a local magnetic moment of an Fe atom dissolved in transition metal alloys of the entire second-row transition metals. The appearance and disappearance of a localized moment resembles somewhat the variation

¹¹⁴ B. S. Chandrasekhar and J. K. Hulm, J. Phys. Chem.

 ¹⁷A Study of the Band Structure and Superconducting Properties of Several γ-Uranium Alloys from Measurements of Their Specific Heats between 1°K and 4°K, Proceedings of the VI1th International Conference on Low Temperature Physics, edited by G. M. Graham and A. C. Hollis Hallett (University of Toronto Press, Canada, 1961), p. 350..
 ¹¹⁷B. T. Matthias, V. B. Compton, H. Suhl, and E. Corenzwit, Phys. Rev. 115, 1597 (1959).

¹¹⁸ B. T. Matthias, J. Appl. Phys. Suppl. **31**, 23S (1960). ¹¹⁹ B. T. Matthias, M. Peter, H. J. Williams, A. M. Clogston, B. T. Matthias, C. Clarker, H. J. Williams, A. M. Clogston, C. Clarker, M. B. T. Matthias, J. Phys. Rev. L 510 (1970). E. Corenzwit, and R. C. Sherwood, Phys. Rev. Letters 5, 542

¹²⁰ A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, E. Corenzwit, and R. C. Sherwood, Phys. Rev. 125, 541 (1962).

of the transition temperature with valence-electron concentration. However, the maxima for the magnetic-moment plot coincide with the minima for the transition-temperature plot.

An interesting case is the depression of the transition temperature of Ru by the addition of small amounts of Cr, up to 20 at. % Cr, which also seems to be due to a magnetic interaction. For higher concentrations of Cr the magnetic interaction disappears, as had been observed in the Cr-Ir system, and for Ru solid solutions containing more than 30 at. %Cr the variation in transition temperature with composition is in accord with the empirical rules.¹¹¹

The effect of magnetic rare-earth elements on the superconducting transition temperature of La has been investigated in detail.^{121,122} The lowering of the transition temperature by the rare-earth element seems to be correlated chiefly with the projection of the spin on the orbit of the solute atoms and not with an increase of the effective moment.¹²¹ The effective magnetic moments and spins of the rare-earth elements follow Van Vleck's¹²³ well-known curve, given in Fig. 2. The superconducting transition tem-



FIG. 2. Effective magnetic moments and spins of the rare earth elements¹²³

peratures of solid solutions of La containing 1 at. %of rare-earth element are shown in Fig. 3. It was also concluded from these studies that the depression was essentially symmetrical with respect to Gd. The results of additional studies indicate that a deviation from the symmetrical behavior occurs in La-Nd and in La-Er solid solutions.¹²² The transition temperature of La is lowered much more rapidly by Nd than by Er. Both elements have the same spin but the ef-



FIG. 3. Superconducting transition temperatures of 1 at. % rare earth solid solutions in La¹²¹.

fective magnetic moment of Er is much larger than that of Nd. Here again a larger effective moment increases the transition temperature rather than decreasing it. Theoretical calculations¹²⁴⁻¹²⁶ which attribute the lowering of the transition temperature by the rare-earth solute to the lowering of the free energy of the normal state by the polarized spins give a reasonable interpretation of the data.

Transition-nontransition elements. The superconducting transition temperature is always lowered by the formation of solid solutions between transition and nontransition elements, regardless of how Nvaries. For example, the transition temperature of Nb is increased by solid-solution formation with any transition element with N < 5. The addition of Zr (N = 4) raises the transition temperature to about 11°K for a solid solution containing 20 to 30 at. % $Zr_{,108}$ whereas the addition of Sn (N = 4) lowers the transition temperature to 5.6°K for a solid solution containing 8 at. % Sn.82

2. Intermediate Phases

Nontransition elements. The variation of transition temperature with composition has been studied for

¹²¹ B. T. Matthias, H. Suhl, and E. Corenzwit, Phys. Rev. Letters 1, 92 (1958). ¹²² B. T. Matthias, H. Suhl, and E. Corenzwit, J. Phys.

Chem. Solids 13, 156 (1960). ¹²³ J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, (Oxford University Press, London, 1932), p.

 ¹²⁴ W. Baltensperger, Helv. Phys. Acta **32**, 197 (1959).
 ¹²⁵ H. Suhl and B. T. Matthias, Phys. Rev. Letters **2**, 5

^{(1959).} ¹²⁶ A. Maradudin and J. Peretti, Compt. Rend. **248**, 2856 (1959).

alloys in the In-Sn system.¹²⁷ The system contains two intermediate phases, β and γ . The β phase has an ideal composition of In₃Sn and exists over a wide range of composition from about 14 to 28 at. % Sn. The hexagonal γ phase, InSn₄, has a homogeneity range from about 78–90 at. % Sn. According to the literature the structure of the β phase is still somewhat uncertain. A maximum in the transition temperature occurs at 7.30°K for the β alloy In_{0.70} $Sn_{0.30}$. This composition corresponds to a valenceelectron-per-atom ratio of 3.3. Meissner¹²⁸ reports that In_{0.75} Sn_{0.25} has a transition temperature of 5.5°K.

According to the results of Merriam and Jensen,⁹⁷ it would seem that the valence-electron concentration is relatively unimportant in determining the occurrence of superconductivity in alloys of nontransition elements. Superconductivity will always occur, regardless of crystal structure and composition, whenever the valence-electron concentration is considerably greater than one.

Transition elements. The occurrence of superconductivity in intermediate phases between transition elements is in accordance with the empirical rules stated previously. Superconducting intermediate phases of Cr with Rh and with Ir have been reported.¹¹¹ In both systems the two cubic elements form a superconducting hexagonal close-packed allow which has a homogeneity range. The maximum transition temperature for the Cr-Rh intermediate phase is 1.1°K for a Cr_{0.70}Rh_{0.30} alloy (6.9 valence electrons) and also for a Cr0.75Rh0.25 alloy (6.75 valence electrons); for the Cr-Ir phase, it is 0.83°K for a Cr_{0.72} Ir_{0.28} alloy (6.84 valence electrons).

The hexagonal close-packed intermediate phases in the Mo-Rh,²⁷ Mo-Pd,⁸² Mo-Ir,²⁵ and W-Rh²⁷ systems are superconducting. The transition temperature for a Mo_{0.50}Rh_{0.50} alloy is 1.97°K; for a $Mo_{0.50}Pd_{0.50}$, $3.52^{\circ}K$; $Mo_{0.60}Ir_{0.40}$, $8.4^{\circ}K$ and for W_{0.50}Rh_{0.50}, 2.64°-3.37°K.

Blaugher, Taylor, and Hulm¹¹³ report that a Re alloy containing 33 at. % Hf, which is in the hexagonal region of the phase diagram, has a transition temperature of 5.61°K.

3. Compounds

The influence of crystal structure on superconductivity is more pronounced in compounds than in solid solutions or in intermediate phases, particularly if the compound contains at least one transition element. The crystal structures which are particularly

favorable for superconductivity include the cubic β -W type structure (A15), the cubic NaCl type (B1) and the cubic $MgCu_2$ type (C15). With the exception of NbC and NbN, which have the B1 type structure, most of the high-temperature superconductors have the β -W type structure. However, not all cubic crystal structures are favorable; for example, the CsCltype structure (B2) has been shown to be one of the least favorable.

To date only one superconductor has been found in the trigonal system, PdTe₂,¹²⁹ and only one in the monoclinic system, α -Bi₂Pd.¹³⁰⁻¹³⁴ The occurrence of superconductivity in orthorhombic compounds is not too common-only thirteen have been reported to date.

In order to facilitate the discussion of the superconducting behavior of compounds, they have been arranged and tabulated according to their crystalstructure types. Both superconductors and nonsuperconductors whose crystal structures have been identified are included. In addition to the compounds reported in the literature, the results of our recent investigations of the occurrence of superconductivity in compounds particularly in the temperature range of 0.35 to 1.0° K are also given. The crystal structures of these compounds were identified from x-ray diffraction powder photographs and the observed intensities were compared with those published or with those calculated from the published structural data.

Several new compounds were discovered in the course of our studies. These include ScAl₂, VZn₃, ZrCuAl,¹³⁵ Zr₃Au, Zr₃Pb, and NbVCo. ScAl₂, ZrCuAl, and Zr₃Au were prepared by reacting appropriate amounts of the elements in an arc furnace; Zr₃Pb and NbVCo by reacting the elements in an arc furnace followed by annealing at about 900°C; and VZn₃ by reacting the elements in a quartz tube at 900°C. Both ScAl₂ and ZrCuAl have the cubic MgCu₂-type structure (C15) and neither is superconducting above 1.02°K; VZn₃ has the cubic Cu₃Au-type structure (Ll₂) and is not superconducting above 1.02°K; Zr₃Au has the tetragonal sigma phase-type structure $(D8_b)$ and is not superconducting above 1.02° K; and Zr₃Pb

- ¹³⁰ N. E. Alekseevskii, N. B. Brandt, and T. I. Kostina, Izvest. Akad. Nauk S.S.S.R., Ser. Fiz. 16, 233 (1952).
 ¹³¹ N. E. Alekseevskii, Zh. Eksp. i Teoret. Fiz. 23, 484 (1952).
 ¹³² N. N. Zhuravlev and G. S. Zhdanov, Zh. Eksp. i Teoret.
- Fiz. 25, 485 (1953). ¹³³ N. E. Alekseevskii, N. N. Zhuravlev, and I. I. Lifanov, Zh. Eksp. i Teoret. Fiz. 27, 125 (1954).
 ¹³⁴ N. N. Zhuravlev, Soviet Phys.—JETP 5, 1064 (1957).

¹²⁷ J. H. Wernick and B. T. Matthias, J. Chem. Phys. 34, 2194 (1961). ¹²⁸ H. Meissner, Phys. Rev. **109**, 686 (1958).

¹²⁹ J. Guggenheim, F. Hulliger, and J. Müller, Helv. Phys. Acta 34, 408 (1961).

¹³⁵ E. A. Wood suggested the preparation of this compound and correctly predicted that it would have the C15 type structure.

has the cubic β -W type structure (A15) and is superconducting at 0.76°K. The sigma phase Zr₃Au compound has the cubic β -W type structure (A15), as reported^{136,137} after an anneal at 900°C and has a transition temperature of 0.91°K. NbVCo has the hexagonal $MgZn_2$ -type structure (C14) and is not superconducting above 1.02°K.

 TABLE II. Superconductivity and crystal-structure data for compounds with the A2-type structure.

	Supe	rcondu	ctivity data	Crystal-structure data		
Compound	<i>T</i> ^a ⁰K	${}^{T^b_n}_{ m K}$	References	Lattice constants <i>a</i> ,Å	References	
TiFe TiCo TiNi	0.71	$\begin{array}{c} 0.30\\ 1.02 \end{array}$	82 82 82	$2.973 \\ 2.99 \\ 3.02$	37,82,138 37,82,138 37,82,138 37,82,138	

^a Superconducting transition temperature. ^b The compound exhibited no superconductivity above this temperature.

A2, W-type, body-centered cubic. The superconductivity and crystal structure data for TiFe, TiCo and TiNi which have a disordered body-centered cubic, W type, structure are given in Table II (references 37, 82, and 138). Of these only TiCo is superconducting and has a transition temperature of 0.71°K.

A12, α -Mn-type, body-centered cubic. This is considered a favorable structure for the occurrence of superconductivity in transition metal compounds since all the A12-type binary compounds with suitable valence-electron concentrations, investigated to date, are superconducting. These include compounds of Tc with Zr and with Nb, compounds of Pd with Nb, compounds of Re with Ti, Zr, Nb, Mo, Hf, Ta, and W, and compounds of Os with Nb and with Ta. The transition temperatures of compounds in this structure type range from 1.58°K for Ta_{0.35} Re_{0.65} to 10.5°K for NbTc₃. The superconductivity and crystal structure data are given in Table III (references 60, 82, 113, and 139–143).

A15, β -W type, cubic. This is by far the most favorable crystal structure for the occurrence of superconductivity not only because of the large number of A15type superconducting compounds, but also because the transition temperatures of many of the compounds are above 10°K. The compound Nb₃Sn which has the highest transition temperature known, 18.05°K, crystallizes in this structure.

The formation of solid solutions between superconducting compounds with this structure always results in a lowering of the transition temperature of the compound with the higher temperature. For example, V₃Si and V₃Ga are superconducting at 17.1 and 16.5°K, respectively, and yet the transition temperature of $V_3(Si_{0.5}Ga_{0.5})$ is 8.6 to 11.9°K.⁸² This effect also occurs in solid solutions of Nb₃Al and Nb₃Sn whose transition temperatures are 17.5 and 18.05°K, respectively. A solid solution with the composition $Nb_{3}(Al_{0.5}Sn_{0.5})$ has a transition temperature of 16.3°K.⁸² The transition temperature of Nb₃Sn is

TABLE III. Superconductivity and crystal-structure data for compounds with A 12-type structure.

	Supercond	luctiv	ity data	Crystal-structure data		
Compound	${T_c}_{^\circ m K}$	${}^{T_n}_{^{\circ}\mathrm{K}}$	Refer- ences	Lattice constants a, Å	References	
MgaAla		0.35	. 82	10.55	82.139	
TisRea	6.6		140	9.587	140	
Tio 17Reo 83	5.1		141	9.595	141	
V ₃ Fe ₅ Si ₂	012	0.37	82	8.851	82.142	
V2.8C05.2Si2		1.02	82	8.774	82,142	
V ₃ Ni ₅ Ge ₂		0.35	82	8.928	82,142	
ZrTc ₆	9.7		60	9.636	60	
$ZrRe_6$	7.4		140	9.698	140	
NbTc ₃	10.5		60	9.625	60	
Nb0.60Pd0.40	2.04 - 2.47		141	9.77	141	
Nb0.40Re0.60	2.36		141	9.781	141	
Nb0.18Re0.82	9.7; 8.89		140;143	9.641	140;143	
NbOs	2.86		141	9.760	141	
$NbOs_2$	2.52		140	9.655	140	
$MoRe_3$	9.26		143		143	
Hf0.50Re0.50		1.02	113		113	
Hf0.14Re0.86	5.86		113		113	
Ta0.36Re0.64	1.46		140	9.765	140	
Ta0.35Re0.65	1.58		141	9.762	141	
TaRe ₃	6.78		143		143	
TaOs	1.95		140	9.773	140	
WRe ₃	9.00		143		143	

lowered by the formation of solid solutions with V₃Sn,¹⁴⁴ with V₃Sn-Ta₃Sn,¹⁴⁴ with Nb₃Ga,⁸² and with

 ¹³⁶ M. V. Nevitt, Trans. AIME 212, 350 (1958).
 ¹³⁷ K. Schubert, M. Balk, S. Bhan, et al., Naturwissenschaften 46, 647 (1959).

 ¹³⁸ P. Duwez and J. L. Taylor, J. Metals 2, 1173 (1950).
 ¹³⁹ F. Laves, K. Löhberg, and P. Rahlfs, Nachr. Ges. Wiss. Göttingen. Jahresber. Geschäftsjahr. Math.–Physik Kl. 1, 67

¹⁴⁰ B. T. Matthias, V. B. Compton, and E. Corenzwit, J. Phys. Chem. Solids 19, 130 (1961).
 ¹⁴¹ E. Bucher, F. Heiniger, and J. Müller, Helv. Phys. Acta

³⁴, 843 (1961). ¹⁴² E. I. Gladyshevskii, P. I. Kripyakevich, M. Yu. Teslyuk,

et al., Soviet Phys.—Cryst. 6, 207 (1961). ¹⁴³ R. D. Blaugher and J. K. Hulm, J. Phys. Chem. Solids

^{19, 134 (1961).}

¹⁴⁴ G. D. Cody, J. J. Hanak, G. T. McConville, and F. D. Rosi, "Superconducting Properties of the (NbTaV)₃Sn System," *Proceedings of the VI1th International Conference on* Low Temperature Physics, edited by G. M. Graham and A. C. Hollis Hallett (University of Toronto Press, Canada, 1961), p. 382.

Ta₃Sn.^{144–146} Recently, the superconducting behavior of the binary systems Nb₃Al-Nb₃Sb¹⁴⁷ and Nb₃Sn-Nb₃Sb¹⁴⁸ has been studied as a function of composition.

In addition, it has not been possible to raise the transition temperature of an A15-type superconductor by the addition of other elements. For example, Hardy and Hulm¹⁴⁹ found that the transition temperature of V₃Si was always lowered when part of the V or Si was replaced by other elements.^{149a}

The superconductivity and crystal-structure data for A15 structure-type compounds are given in Table IV (references 25, 27, 82, 111, 112, 136, 137, 140, 141, 144, and 149–163).

B1, NaCl type, face-centered cubic. The only superconducting compounds with this type structure are the interstitial carbides and nitrides. Giorgi and coworkers¹⁶⁴ studied the transition temperatures of NbC and TaC as a function of composition and found that the highest temperature is reached for the stoichiometric compositions. In the case of NbC the composition ranged from $NbC_{0.977}$ which has a transition temperature of 11.1°K to NbC_{0.70} which is not superconducting above 1.05°K. For TaC the composition ranged from $TaC_{0.987}$ with a transition temperature of 9.7° K to TaC_{0.754} which is not superconducting above 1.05°K. Rögener¹⁶⁵ investigated the transition temperature of NbN as a function of composition and re-

¹⁴⁵ H. J. Jansen and E. J. Saur, "Superconductivity in the System Niobium-Tin," *Proceedings of the VII International Conference on Low Temperature Physics*, edited by G. M. Graham and A. C. Hollis Hallett (University of Toronto Press, 1997) Canada, 1961), p. 379.

¹⁴⁶ H. G. Jansen, Z. Physik 162, 275 (1961).
 ¹⁴⁷ F. Rothwarf, C. C. Dickson, E. Parthé, and H. Boller, Bull. Am. Phys. Soc. 7, 322 (1962).
 ¹⁴⁸ T. B. Reed and H. C. Gatos, Bull. Am. Phys. Soc. 7, 322

(1962).

¹⁴⁹ G. F. Hardy and J. K. Hulm, Phys. Rev. 93, 1004 (1954). ^{149a} Note added in proof. This has recently been confirmed by N. E. Alekseevskii et al. [Doklady Akad. Nauk SSSR 145, 82

- N. E. Alekseevskii et al., 1990, 1991
 (1962)].
 ¹⁵⁰ P. Duwez and C. B. Jordan, Acta Cryst. 5, 213 (1952).
 ¹⁵¹ P. Duwez, J. Metals 3, 564 (1951).
 ¹⁵² E. A. Wood, V. B. Compton, B. T. Matthias, and E. Corenzwit, Acta Cryst. 11, 604 (1958).
 ¹⁵³ P. Greenfield and P. A. Beck, J. Metals 8, 265 (1956).
 ¹⁵⁴ S. Geller, B. T. Matthias, and R. Goldstein, J. Am. Chem.
- ¹⁵⁰ S. Gener, D. I. Matthias, and R. Goldstein, J. All. Chem.
 Soc. 77, 1502 (1955).
 ¹⁵⁵ E. A. Wood and B. T. Matthias, Acta Cryst. 9, 534 (1956).
 ¹⁵⁶ E. Corenzwit, J. Phys. Chem. Solids 9, 93 (1959).
 ¹⁵⁷ J. H. Carpenter and A. W. Searcy, J. Am. Chem. Soc. 78,
- 2079 (1956).

2079 (1956).
¹⁵⁸ M. D. Banus, T. B. Reed, H. C. Gatos, et al., J. Phys. Chem. Solids 23, 971 (1962).
¹⁵⁹ B. T. Matthias, T. H. Geballe, S. Geller, and E. Corenz-wit, Phys. Rev. 95, 1435 (1954).
¹⁶⁰ W. Wiedmann, Z. Physik 151, 307 (1958).
¹⁶¹ E. Raub, Z. Metallk. 45, 23 (1954).
¹⁶² A. G. Knapton, J. Inst. Metals 87, 28 (1958).
¹⁶³ S. Geller, Acta Cryst. 9, 885 (1956).
¹⁶⁴ A. L. Giorgi, E. G. Szklarz, E. K. Storms, Allen L. Bowman, and B. T. Matthias, Phys. Rev. 125, 837 (1962).

- ¹⁶⁵ H. Rögener, Z. Physik **132**, 446 (1952).

ported that NbN_{0.96} has a transition temperature of 15.63°K.

The face-centered cubic carbides of Ti, V, and Zr, which are normal down to 1.20°K, will form superconducting solid solutions with hexagonal MoC. The transition temperature of NbC is also raised to 12.50°K by solid-solution formation with MoC.¹¹² The transition temperatures of the B1-type solid solutions are:

$(TiC)_{0.17}(MoC)_{0.83}$	$10.20^{\circ}\mathrm{K}$
$(VC)_{0.20}(MoC)_{0.80}$	9.30
$({\rm ZrC})_{0.17} ({ m MoC})_{0.83}$	9.50

TABLE IV. Superconductivity and crystal-structure data for compounds with A15-type structure.

	Supercond	luctiv	ity data	Crystal-stru	ucture data
Compound	<i>T₅</i> °K	$_{^{\circ}\mathrm{K}}^{T_{n}}$	Refer- ences	Lattice constants a, Å	References
Ti-Sh	5.9		140	5 917	140
TiaIr	5.0		140	5 000	140
TioPt	0.58		82	5.000	82 150
TieAu	0.00	1.20	149	0.002	140
VaSi	171	1.20	149	4 722	149
V ₃ Co	11.1	0.35	82	4 684	82 151
VaGa	16.5	0.00	112 152	4 816	152
VaGe	6.01		149	1.010	149
V.As	0.01	1.02	112	4 74	112
V.Rh	0.38	1.02	82	4.784	82 153
VaSn	7.0		154	4 94	154
1 3~11	3.8		144	4.96	144
V ₂ Sb	0.80		82	4.941	82 136 152
VaIr	0.00	0.35	$\tilde{82}$	4.786	82,136,163
(V2 67 Iro 23) Ir	1.39	0.00	140	4.794	140
V ₃ Pt	2.83		140	4.814	140
VaAu	0.74		82	4.883	82 155
Cr ₈ Si		1.20	149		149
Cr ₂ Ga		0.35	82	4.645	82.152
Cr ₃ Ge		1.20	149		149
Cr ₃ Ru	3.3		111		ĨĨĨ
Cr ₃ Rh		0.30	111		111
Cr0.85 Ir0.15	0.77	•	111		111
Cr ₃ Pt		0.30	111		111
Zr ₃ Au	0.92		82	5.483	82.136.137
Zr ₃ Pb	0.76		82	5.656	82
Nb ₃ Al	17.5		152	5.187	152
	16.8 - 18.0		156, a		156, a
Nb3Ga	14.5		152	5.171	152^{-1}
Nb₃Ge	6.90		82	5.166	82,136,157
Nb₃Rh	2.50		112	5.115	112
Nb3In	9.2		158	5.303	158
Nb_3Sn	18.05		159,160	5.289	154
Nb_3Sb		1.02	112,152	5.262	152
$Nb_{3}Os$	1.05		112	5.121	154
$Nb_{3}Pt$	9.2		154	5.153	154
$Nb_{3}Ir$	1.7		154	5.131	154
Nb ₃ Au	11.5		155	5.21	155
Mo ₃ Al	0.58		82	4.950	82,152
Mo ₃ Si	1.30		149		149
Mo ₃ Ga	0.76		82	4.943	82,152
Mo ₃ Ge	1.43		149		149
Mo ₃ Os	7.2		27		27
Mo ₃ lr	8.35; 8.8		25;27	4.974	82,161,162
$M_{00.74} Ir_{0.26}$	9.05		141	4.972	141
$1a_3Sn$	6.0		154,159	5.276	154
	6.4		144	5.278	144

^a Note added in proof. K. Raetz and E. Saur, Z. Physik 169, 315 (1962).

The transition temperature of NbN is raised by the formation of a solid solution with NbC and a transition temperature of 17.8°K is reported for NbN containing 25 to 30 at. % NbC.¹⁰⁸

Hardy and Hulm¹⁴⁹ studied the effect of oxygen on the transition temperatures of Ti, V, and Zr nitrides and found that the transition of TiN and VN are affected by the presence of oxygen in the sample, whereas that of ZrN is not. Schröder¹⁶⁶ also found that oxygen lowered the transition temperature of NbN and reported that $Nb(N + O)_{0.97}$ has a transition temperature of 7.66°K.

The superconductivity and crystal-structure data for B1-type compounds are listed in Table V (references 82, 149, 164, 165, and 167-176).

TABLE V. Superconductivity and crystal-structure data for compounds with B1-type structure.

	Supercond	Superconductivity data			Crystal-structure data		
Compound	<i>T₅</i> °K	${}^{T_n}_{^{\circ}\mathrm{K}}$	Refer- ences	Lattice constants <i>a</i> ,Å	References		
ScN		1.40	167	4.45	167		
TiC		1.20	149		149		
TiN	5.6; 4.86		149:168		149:168		
TiO	,	1.20	149		149		
VC		1.20	149		149		
VN	8.2;7.5		149:168		149:168		
VO		1.20	149		149		
CrN		1.28	168		168		
YSb		1.02	82	6.161	82.169		
YTe		1.02	82	6.120	82,169		
ZrC		1.20	149		149		
ZrN	8.9; 9.05		149;168		168		
	10.7		176		a		
$NbC_{0.977}$	11.1		164		164		
$\rm NbC$	6.0; 10.3		149;170	4.40	170		
$NbN_{0.96}$	15.63		165	4.377 - 4.381	165		
NbN	14.7; 16.0		168;171	4.38	171		
NbO		1.20	149		149		
$LaN_{0.99}$		1.8	172	5.295	172		
LaSb		1.02	82	6.498	82,173		
CeBi		1.28	168	6.487	174		
\Pr{Bi}		ь	174	6.448	174		
${ m HfN}$	6.2		176		a		
$\mathrm{TaC}_{0.987}$	9.7		164		164		
TaC	2.40 - 3.55		175	4.455	175		
UC		1.20	149	4.952	149		
UN		1.20	149		149		

^a See section on superconducting compounds of unknown structure. ^b Not stated.

B2, CsCl type, cubic. Superconductivity and crystal

structure data for compounds with this type structure are given in Table VI (references 37, 82, 140, and 177-181). Only TiRu and TiOs are superconducting at 1.07 and 0.46°K, respectively.¹⁸¹ This structure is considered to be one of the least favorable for the occurrence of superconductivity.

TABLE VI. Superconductivity and crystal-structure data for compounds with B2-type structure.

	Superc	onducti	vity data	Crystal-structure data		
Compound	<i>T</i> ^c °K	$^{T_n}_{^{\circ}\mathrm{K}}$	Refer- ences	Lattice constants a, Å	References	
MgRh		1.02	177	3.099	178	
MgAg		1.02	82	3.31	37.82.179	
MgAu		0.35	82	3.252	37.82	
AlŎs	0.39		82		140	
\mathbf{ScRh}		1.02	177	3.206	178	
SePt		1.02	140		140	
TiRu	1.07		82	3.067	82.180	
TiOs	0.46		82	3.077	82.180	
VOso.40		0.37	82		140	
HfRu		1.02	82	3.22	82,181	

B81, NiAs type, hexagonal. Most NiAs type compounds that have favorable valence-electron concentrations and are not ferromagnetic are superconducting. The data for $B8_1$ -type compounds are given in Table VII (references 37, 82, 108, 130, 168, 174, and 182-189).

- ¹⁷¹ W. T. Ziegler and R. A. Young, Phys. Rev. 90, 115 (1953)
- ¹⁷² Ŕ. A. Young and W. T. Ziegler, J. Am. Chem. Soc. 74, 5251 (1952). ¹⁷³ A. Iandelli and E. Botti, Atti. Accad. Naz. Lincei, Rend.,
- Classe sci. fis., mat. e nat. 25, 498 (1937). ¹⁷⁴ N. N. Zhurayley, G. S. Zhdanov, and N. E. Alekseevksii,
- Vestn. Mosk. Univ., Ser. Mat., Mekhan., Astron., Fiz. i Khim. 14, 117 (1959). ¹⁷⁵ G. Lautz and D. Schneider, Z. Naturforsch. 17A, 54
- (1962). ¹⁷⁶ E. G. Szklarz and A. L. Giorgi, Bull. Am. Phys. Soc. 7, (1962).
 ¹⁷⁷ B. T. Matthias and E. Corenzwit (private communica-

tion) quoted in reference 178. ¹⁷⁸ V B Compton Act C

- . B. Compton, Acta Cryst. 11, 446 (1958)
- ¹⁷⁹ H. R. Letner and S. S. Sidhu, J. Appl. Phys. 18, 833
- (1947). ¹⁸⁰ C. B. Jordan, J. Metals 7, 832 (1955). Trans. AIME 215, 283 ¹⁸¹ A. E. Dwight, Trans. AIME **215**, 283 (1959).

^{181a} Note added in proof. Recently, we have found that AlOs

- is superconducting at 0.39 °K. ¹⁸² B. T. Matthias (private communication) quoted in reference 183
- ¹³³ S. Geller, J. Am. Chem. Soc. 77, 2641 (1955).
 ¹⁸⁴ V. P. Glagoleva and G. S. Zhdanov, Zh. Eksp. i Teoret.
- Fiz. 25, 248 (1953).
 ¹⁸⁵ B. T. Matthias, E. Corenzwit, and C. E. Miller, Phys. Rev. 93, 1415 (1954).
 ¹⁸⁶ S. Geller and B. T. Matthias, J. Phys. Chem. Solids 4,
- 156 (1958).
- Matthias, Phys. Rev. 90, 487 (1953).
- ¹⁸⁸ W. O. J. Groeneveld Meijer, Am. Mineralogist 40, 646 (1955). ¹⁸⁹ N. N. Zhuravlev and L. Kertes, Soviet Phys.—JETP 5,
- 1073 (1957).

 ¹⁶⁶ E. Schröder, Z. Naturforsch. **12A**, 247 (1957).
 ¹⁶⁷ W. Meissner and H. Franz, Z. Physik **65**, 30 (1934).
 ¹⁶⁸ B. T. Matthias and J. K. Hulm, Phys. Rev. **87**, 799 (1952).

 ⁽¹⁹⁵²⁾.
 ¹⁶⁹ A. Iandelli, "Cell Dimensions and Magnetical Susceptibilities of the MX Compounds of Rare Earths with P, As, Sb, Bi, S, Se, Te," *Rare Earth Research*, edited by E. V. Kleber (The Macmillan Co., New York, 1961), p. 135.
 ¹⁷⁰ F. H. Horn and W. T. Ziegler, J. Am. Chem. Soc. 69, 0720 (1977)

^{2762 (1947)}

B10, PbO type, tetragonal. Jones and Ittner¹⁹⁰ report that BiIn which has this type structure is not superconducting above 1.55°K.

B11, γ -CuTi type, tetragonal. γ CuTi is not superconducting above 1.02°K.82

TABLE VII. Superconductivity and crystal-structure data for compounds with B81-type structure.

	Supe	ercond dat	uctivity a	Crystal-structure data		
Compound	<i>Те</i> °К	${}^{T_n}_{^{\circ}\mathrm{K}}$	Refer- ences	Lat const a,Å	tice ants <i>c</i> ,Å	Refer- ences
CrSb		1.00	108			108
MnSb		1.00	108			108
MnBi		1.28	168			168
CoTe		1.00	108			108
NiSb		0.35	82	3.942^{a}	5.155^{a}	37,82
NiTe		1.00	108			108
NiBi	4.25		130	4.070	5.35	174
RhTe		1.06	182	3.99	5.66	183
RhBi	2.06		130.184	4.094	5.663	184
(Pdo 75Nio 25)As	1.6		185	3.66	5.03	186
PdSb	1.5		108, 187			108, 187
PdTe	2.3		108,187			108,187
IrTe		0.35	82	3.930ª	5.386^{a}	82,188
PtSb	2.1		108, 187			108,187
PtBi	1.21		187,189	4.315	5.49	174
	2.4		174	4.20	5.55	174

^a Powder patterns in present investigation were indexed based on these reported lattice constants.

B18, CuS type, hexagonal. The compounds CuS and CuSe crystallize in this structure type, and their superconducting properties have been investigated. CuS is superconducting at 1.66°K,¹⁹¹ and CuSe is not superconducting above 1.28°K.¹⁶⁸

B20, FeSi type, cubic. The only superconducting compound with this type structure is AuBe. A number of other compounds with favorable valence-electron concentrations are not superconducting in the temperature range measured. The data for B20-type compounds are given in Table VIII (references 82, 149, and 192-195).

B31, MnP type, orthorhombic. This structure is a distortion of the NiAs-type structure $(B8_1)$ and seems to be favorable for the occurrence of superconductivity. The superconductivity and crystal-structure data for B31-type compounds are listed in Table IX (references 82, 108, 187, 194, 197, and 198). Three

- ¹⁹⁴ W. L. Korst, L. N. Finnie, and A. W. Searcy, J. Phys. Chem. 61, 1541 (1957).
 ¹⁹⁵ B. T. Matthias, J. Phys. Chem. Solids 10, 343 (1959).

superconducting compounds are known, namely, PdSi, IrGe, and PtSi.^{198a} Since both RhGe and IrGe have the same number of valence electrons, the difference in their superconducting behavior is somewhat surprising; RhGe is not superconducting above

TABLE VIII. Superconductivity and crystal-structure data for compounds with B20-type structure.

	Super	condu	ctivity data	Crystal-structure data		
Compound	<i>T</i> °K	^T ⁿ °K	References	Lattice constants a, Å	References	
CrGe RhSi Pd4Al3Si OsSi AuBe	2.64	$1.20 \\ 0.35 \\ 1.02 \\ 0.60$	$149 \\ 82 \\ 82 \\ 82 \\ 195$	$\begin{array}{c} 4.673 \\ 4.840 \\ 4.728 \end{array}$	$149 \\82,192 \\82,193 \\82,193 \\82,194 \\195$	

1.00°K, 196 and IrGe is superconducting at 4.7°K. This was another indication that the assignment of the same number of valence electrons to all the elements in the same column of the periodic system was an oversimplification. In general, the number of valence electrons for the 5d elements seems to be shifted somewhat to the right with respect to the corresponding 4d elements.

TABLE IX. Superconductivity and crystal-structure data for compounds with B31-type structure.

	Sup	ercono dat	luctivity	Crystal-structure data			
Com- pound	$^{T_{e}}_{^{\circ}\mathrm{K}}$	$^{T_n}_{^{\circ}\mathrm{K}}$	Refer- ences	Latti <i>a</i> ,Å	ice const b,Å	ants <i>c</i> ,Å	Refer- ences
RhGe RhSb PdSi PdGe IrSi IrGe PtSi PtGe AuGa	0.93 4.7 0.88 0.40	$\begin{array}{c} 0.96 \\ 0.35 \\ 0.35 \\ 1.02 \end{array}$	82 82 82 82 82 108,187 82 82 82 82	$\begin{array}{c} 5.70^{a}\\ 6.340^{a}\\ 6.133^{a}\\ 6.259^{a}\\ 5.558^{a}\\ 5.932^{a}\\ 6.088^{a}\\ 6.397^{a}\\ \end{array}$	$\begin{array}{c} 6.48^{a} \\ 5.955^{a} \\ 5.599^{a} \\ 5.782^{a} \\ 3.211^{a} \\ 5.595^{a} \\ 5.733^{a} \\ 6.266^{a} \end{array}$	$\begin{array}{c} 3.25^{a} \\ 3.876^{a} \\ 3.381^{a} \\ 3.481^{a} \\ 6.273^{a} \\ 3.603^{a} \\ 3.701^{a} \\ 3.421^{a} \end{array}$	$\begin{array}{r} 82,197\\ 82,198\\ 82,198\\ 82,198\\ 82,198\\ 82,194\\ 108,187\\ 82,198\\ 82,198\\ 82,198\\ 82,198\end{array}$

^a Powder patterns in present investigation were indexed based on these reported lattice constants.

 B_t , ζ -CrB type, orthorhombic. The B_t -type compound NbB is the only reported superconductor with this structure. The data are given in Table X (references 149 and 168).

¹⁹⁰ R. E. Jones and W. B. Ittner, Phys. Rev. 113, 1520 (1959).
 ¹⁹¹ W. Buckel and R. Hilsch, Z. Physik **128**, 324 (1950).
 ¹⁹² S. Geller and E. A. Wood, Acta Cryst. **7**, 441 (1954).
 ¹⁹³ K. Schubert, W. Burkhardt, P. Esslinger, *et al.*, Naturwissenschaften **43**, 248 (1956).

¹⁹⁶ B. T. Matthias (private communication) quoted in reference 197.

 ¹⁹⁷ S. Geller, Acta Cryst. 8, 15 (1955).
 ¹⁹⁸ H. Pfisterer and K. Schubert, Z. Metallk. 41, 358 (1950).
 ¹⁹⁸ Note added in proof. RhGe and PtGe are also superconducting at 0.96 and 0.40k, respectively.

 B_a , MoB type, tetragonal. MoB and WB crystallize in this type structure and are not superconducting above 1.28°K.168

 B_h , WC type, hexagonal. MoP and WC are not

TABLE X. Superconductivity and crystal-structure data for compounds with B_{f} -type structure.

	Sup	Superconductivity data			Crystal-structure data			
Com- pound	<i>T₀</i> °K	$^{T_n}_{^{\circ}\mathrm{K}}$	Refer- ences	Latt $a, Å$	ice cons b,Å	tants <i>c</i> ,Å	Refer- ences	
VB CrB NbB MoB TaB	8.25	$1.20 \\ 1.28 \\ 1.28 \\ 1.28 \\ 1.28$	$149\\168\\168\\168\\168\\168$	3.058	8.026	2.971	$149\\168\\168\\168\\168\\168$	

superconducting above 1.03¹⁸⁵ and 1.28°K,¹⁶⁸ respectively.

 $B_i, \gamma' - MoC type, hexagonal.$ Schröder¹⁶⁶ found that NbN remained normal down to 1.94°K. The lattice constants of the sample were a = 2.950 Å and c = 11.252 Å.

C1, CaF₂ type, face-centered cubic. CoSi₂ is the only superconductor reported and has a transition temperature of 1.22°K. The data for C1-type compounds investigated for superconductivity are given in Table XI (references 108, 185, and 199).

C1_b, MgAgAs type, face-centered cubic. Matthias and Hulm¹⁶⁸ report that CuMgBi which crystallizes

TABLE XI. Superconductivity and crystal-structure data for compounds with C1-type structure.

	Su	percon da	ductivity ta	Crystal-structure data		
Compound	°K	<i>T</i> ⁿ ⁰K	References	Lattice constants <i>a</i> ,Å	References	
CoSi ₂	1.22		199		199	
NiSi2		1.00	108		108	
$Rh_2\tilde{P}$		1.03	185		185	
$PtAl_2$		1.00	108		108	
$AuAl_2$		1.00	108		108	

in this structure is not superconducting above 1.28°K.

C2, FeS_2 type, cubic. The superconductivity and crystal structure data for C2-type compounds are given in Table XII (references 27, 82, 174, 183, 185, 186, 188, 189, and 200-202). A number of the compounds have a wide homogeneity range. Superconductivity occurs both in compounds with the ideal composition and also in those which deviate from the ideal 1:2 stoichiometry.

C6, CdI_2 type, trigonal. Recently, Guggenheim, Hulliger and Müller¹²⁹ investigated the superconduct-

TABLE XII. Superconductivity and crystal-structure data for compounds with C2-type structure.

	Sup	ercon da	ductivity ta	Crystal-structure data		
Compound	<i>T</i> ₅ °K	$^{T_n}_{^{\circ}\mathrm{K}}$	$\overset{\text{Lattic}}{\overset{\text{constar}}}{\overset{\text{constar}}{\overset{\text{constar}}{\overset{\text{constar}}}{\overset{\text{constar}}{\overset{\text{constar}}{\overset{\text{constar}}{\overset{\text{constar}}{\overset{\text{constar}}}{\overset{\text{constar}}{\overset{\text{constar}}{\overset{\text{constar}}}{\overset{\text{constar}}{\overset{\text{constar}}}{\overset{\text{constar}}}{\overset{\text{constar}}{\overset{\text{constar}}}{\overset{\text{constar}}}{\overset{\text{constar}}{\overset{\text{constar}}}{\overset{\overset{\text{constar}}}{\overset{s}}}{\overset{s}}{\overset{s}}}{\overset{s}}{\overset{s}}}{\overset{s}}{\overset$		References	
RhSe _{1.75}	6.0		27,185	6.015	27,200	
x-RhTe ₂	1.51		27,185	6.441	183	
Pd _{0.88} Ni _{0.12})As	1.39		186		186	
Pd _{0.75} Ni _{0.25})As	1.34		186		186	
$PdSb_2$	1.25		82	6.459	82,201	
$[rTe_{2.67}]$		0.35	82	6.410	82,188	
μ -PtBi ₂		a	174,189	6.683	174	
AuSb ₂	0.58		82	6.658	82,202	

* Not stated.

ing properties of some C6-type compounds and reported that PdTe₂ is superconducting. This is the only superconductor with this type structure reported to date. The compound has a homogeneity range from PdTe₂ to Pd_{1,75}Te₂ and the corresponding transition temperatures are 1.53 and 2.25°K, respectively. Mixed crystals of PdTe₂ containing small amounts of Ni or Rh or Pt are also superconducting. The compound PdSeTe which crystallizes in this structure is not superconducting above 1.2°K.

The data for C6-type compounds are given in Table XIII (references 129, 182, and 183).

TABLE XIII. Superconductivity and crystal-structure data for compounds with C6-type structure.

	Sup	ercond dat	luctivity a	Crystal-structure data		
Compound	<i>T</i> ₅ °K	$_{^{\circ}\mathrm{K}}^{T_{n}}$	References	Lat cons $a, Å$	tice tants <i>c</i> ,Å	References
$\begin{array}{c} & \text{NiTe}_2 \\ \beta\text{-RhTe}_2 \\ \text{PdTe}_2 \\ \text{PtTe}_2 \end{array}$	1.53	$1.2 \\ 1.06 \\ 1.2$	129 182 129 129	3.92	5.41	$ 129 \\ 183 \\ 129 \\ 129 \\ 129 $

C11b, MoSi₂ type, body-centered tetragonal. Hardy and Hulm¹⁴⁹ report that β -MoGe₂ is not superconducting above 1.20°K.

¹⁹⁹ B. T. Matthias and J. K. Hulm, Phys. Rev. 89, 439 (1953). ²⁰⁰ S. Geller and B. B. Cetlin, Acta Cryst. 8, 272 (1955).

 ²⁰¹ L. Thomassen, Z. Phys. Chem. 135, 383 (1928).
 ²⁰² O. Nial, A. Almin, and A. Westgren, Z. Phys. Chem. **B14**, 81 (1931).

C14, MgZn₂ type, hexagonal (Laves Phase). This structure is favorable for the occurrence of superconductivity. In addition, ferromagnetism also occurs in the C14 rare-earth Laves phases in which the rare-earth atom contains 4f electrons.²⁰³ Solid solutions between C14-type rare-earth compounds with 4f electrons and those without 4f electrons are both superconducting and ferromagnetic simultaneously. Superconductivity and ferromagnetism have been studied in the YOs₂–GdOs₂ system for compositions containing up to 14 at. % GdOs₂ in YOs₂.¹¹⁸

The superconductivity and crystal structure data are given in Table XIV (references 82, 121, 140, and 203 - 208).

 $C15, MgCu_2 type, cubic$ (Laves Phase). Since many compounds with this type structure are superconducting, it is considered a very favorable one. The

TABLE XIV. Superconductivity and crystal-structure data for compounds with C14-type structure.

	Superc	onduc	tivity data	Crystal-structure data			
Com- pound	<i>T₅</i> °K	$^{T_n}_{^{\circ}\mathrm{K}}$	References	Lat cons <i>a</i> ,Å	tice tants <i>c</i> ,Å	References	
CaMg ₂		1.02	82	6.23ª	10.12ª	82,204	
$ScRu_2$	1.67		121,203	5.119	8.542	203	
$ScOs_2$	4.6		203	5.179	8.484	203	
$TiZn_2$		1.02	82	5.064ª	8.210ª	82,205	
YRu_2	1.52		203	5.256	8.792	203	
YRe_2	1.83		203	5.396	8.819	203	
YOs_2	4.7		203	5.307	8.786	203	
$ZrAl_2$	0.30 ^b		82	5.282ª	8.748ª	82,206	
$\rm ZrCr_2$		0.35	82	5.102^{a}	8.239^{a}	82,207	
Zr ₂ VCo ₃		0.35	82	4.982	8.114	82,207	
$ZrRu_2$	1.84		140	5.144	8.504	140	
$ZrRe_2$	6.8		82	5.262^{a}	8.593ª	82,208	
$ZrOs_2$	3.00		140	5.219	8.538	140	
NbVCo		1.02	82	4.928	8.008	82	
$LuRu_2$	0.86		82	5.204	8.725	203	
$LuOs_2$	3.49		203	5.254	8.661	203	
$HfRe_2$	4.8		203	5.239	8.584	203	
$HtOs_2$	2.69		203	5.184	8.468	203	

^a Powder patterns in present investigation were indexed based on these reported lattice constants. ^b Beginning of transition.

data for C15-type compounds are given in Table XV (references 37, 82, 113, 114, 121, 140, 174, 203, 207, and 212-229).

- ²⁰³ V. B. Compton and B. T. Matthias, Acta Cryst. 12, 651 (1959).
 - ²⁰⁴ H. Witte, Naturwissenschaften **25**, 795 (1937).
- ²⁰⁵ P. Pietrokowsky, J. Metals 6, 219 (1954).
 ²⁰⁶ C. G. Wilson, Acta Cryst. 12, 660 (1959).
 ²⁰⁷ R. P. Elliott and W. Rostoker, Trans. Am. Soc. Metals 50, 617 (1958)
- H. J. Wallbaum, Naturwissenschaften **30**, 149 (1942).
 B. T. Matthias, H. Suhl, and E. Corenzwit, Phys. Rev.
- Letters 1, 449 (1958). ²¹⁰ R. M. Bozorth, D. D. Davis, and A. J. Williams, Phys.
- Rev. 119, 1570 (1960).

The simultaneous occurrence of superconductivity and ferromagnetism was investigated by solid-solution formation between a superconducting Laves phase and a ferromagnetic one. The rare-earth systems which have been studied in this respect include the CeRu₂-PrRu₂ and CeRu₂-GdRu₂ C15-type solid solutions^{209,210} and the C15-C14-type LaOs₂-GdOs₂ solid solutions.²¹⁰ These phenomena have also been investigated in the ThRu₂-GdRu₂ solid solutions.²¹¹

CeRu₂ is the only known superconductor which contains a rare-earth element that usually has 4felectrons. However, based on the lattice constant of this compound, it was concluded that most of the 4felectrons have been squeezed into the outer s and dshells.121

 $C15_b$, $AuBe_5$ type, face-centered cubic. No superconducting compounds with this type structure have been reported. The compounds which have been investigated are listed in Table XVI (references 82, 230-232).

C16, $CuAl_2$ type, body-centered tetragonal. The transition temperatures of the isomorphous series of Th compounds with Cu, Ag, and Au indicated, as stated earlier, that the assignment of the same number of valence electrons to all the elements in the same column should be considered as a rough approximation. Since $AgTh_2$ has the optimum volume/ mass ratio, it should have the highest transition

²¹¹ R. M. Bozorth, B. T. Matthias, and D. D. Davis, "Superconductivity and Ferromagnetism in the System GdRu₂-ThRu₂," Proceedings of the VIIth International Con-ference on Low Temperature Physics, edited by G. M. Graham and A. C. Hollis Hallett (University of Toronto Press, Canada, ²¹² W. Haucke, Z. Elektrochem. **43**, 712 (1937).
 ²¹³ H. Perlitz and E. Aruja, Z. Krist. **100**, 157 (1938).
 ²¹⁴ J. B. Friauf, J. Am. Chem. Soc. **49**, 3107 (1927).

- ²¹⁵ N. E. Alekseevskii, Zh. Eksp. i Teoret. Fiz. 20, 863 (1950).
 ²¹⁵ N. N. Zhuravlev, G. S. Zhdanov, and R. N. Kuz'min, Soviet Phys.-Cryst. 5, 532 (1961).
 ²¹⁷ H. Nowotny and A. Mohrnheim, Z. Krist. 100, 540
- (1938)
- ²¹⁸ B. T. Matthias and E. Corenzwit, Phys. Rev. 107, 1558
- (1957). ²¹⁹ E. A. Wood and V. B. Compton, Acta Cryst. 11, 429 (1958).
- ²²⁰ L. Misch, Metallwirt. 15, 163 (1936).
 ²²¹ N. N. Zhuravlev, T. A. Mingazin, and G. S. Zhdanov, Soviet Phys.—JETP 7, 566 (1958).
- ²²² E. E. Cherkashin, E. I. Gladyshevski, et al., Zh. Neorgan. Khim. 3, 650 (1958). ²²³ N. N. Zhuravlev, Soviet Phys.—JETP 7, 571 (1958).
- ²²⁴ F. Laves, Naturwissenschaften **31**, 96 (1943).
 ²²⁵ S. E. Haszko, Trans. AIME **218**, 958 (1960).
- ²²⁶ W. J. de Haas and T. Jurriaanse, Proc. Acad. Sci. Amsterdam **35**, 748 (1932). ²²⁷ T. Jurriaanse, Z. Krist. **90**, 322 (1935).

- J. Jurnaanse, Z. Krist. 90, 322 (1955).
 Za A. E. Dwight, Trans. Am. Soc. Metals 53, 479 (1961).
 T. J. Heal and G. I. Williams, Acta Cryst. 8, 494 (1955).
 L. Misch, Metallwirt. 14, 897 (1935).
 S. S. Sidhu and C. O. Henry, J. Appl. Phys. 21, 1036 (1950)
- ⁽¹²⁰⁰⁾.
 ⁽²³²⁾N. C. Baenziger, R. E. Rundle, A. I. Snow, and A. S. Wilson, Acta Cryst. 3, 34 (1950).

temperature. Actually its transition temperature is lower than that of $CuTh_2$ and that of $AuTh_2$, and this would seem to indicate that the number of valence electrons in Ag is either more or less than that

TABLE XV. Superconductivity and crystal-structure data for compounds with C15-type structure.

	Superco	onduc	tivity data	Crystal-structure data		
Compound	${}^{T_c}_{^{\circ}\mathrm{K}}$	$^{T_n}_{^{\circ}\mathrm{K}}$	References	Lattice constants <i>a</i> ,Å	References	
NaAu ₂		1.02	82	7.814	82,212,213	
MgCu ₂		1.02	82	7.034	37.82.214	
KBi ₂	3.57		215	9.501	174,216	
CaAl ₂		1.02	82	8.035	82.217	
$CaRh_2$	6.4		218	7.525	219	
$CaPd_2$		1.02	218	7.665	219	
CaIr ₂	4.0 - 6.15		218	7.545	219	
$CaPt_2$		1.02	218	7.629	219	
ScAl ₂		1.02	82	7.579	82	
ScIr ₂	1.03		203	7.348	203	
TiBe ₂		1.02	82	6.451	82.220	
RbBi ₂	4.25		221	9.609	221	
SrRh ₂	6.2		218	7.706	219	
SrPd ₂		1.02	218	7.826	219	
SrIr ₂	5.7		218	7.700	$\bar{219}$	
SrPt ₂	0	1.02	$\overline{218}$	7.777	$\bar{219}$	
YAL		1.00	$\bar{2}\bar{0}\bar{3}$	7.860	$\bar{2}\bar{0}\bar{3}$	
YRh ₂		0.35	82	7459	$\bar{2}03$	
YIr.	2.18	0.00	203	7.500-7.520	203	
ŶPt.	1.57		203	7 590	$\bar{2}03$	
ZrCu Ala	1.01	1.02	82	7.322	82	
ZrVa	88	1.01	140	7 439	140	
ZrCo	0.0	1.02	82	6 935	37.82.207	
ZrVo Ni	0.43	1.04	82	7.068	82 222	
ZrMnNi	0.10	0.35	82	7 070	82 222	
ZrWo	2 16	0.00	140	7 621	140	
ZrIro	4 10		140	7 359	140	
CaBia	4 75		223	9 746	223	
BaBha	6.0		218	7 852	219	
BaPda	0.0	1.02	218	7 953	219	
BaPto		1.02	218	7 920	219	
LaMga		1.02	82	8 763	82 224	
LaRue	1.63	1.04	121 203	7 702	203	
LaRha	1.00	1.00	203	7 646	203	
LaOsa	65	1.00	203	7 737	203	
LaIra	0.0	1.00	200	7 686	200	
LaPto		1.00	200	7 763-7 774	203	
CoRus	4.9	1.00	203	7 525	200	
CoRho	т.9	0.35	82	7 538	203	
CeOse		0.00	82	7 593	203	
Colro		0.02	82	7 571	203	
LuAl		1 02	82	7 744	82 225	
HfMos		1.02	112	1.1 11	113	
HfW.		1.02	80	7 504	37.89	
BiAu	1.84	1.02	226	7.054	997	
ThRu.	2.56		140	7.651	140	
ThOse	0.00	1.02	89	7 704	81 998	
ThIr.	65	1.02	140	7 661	1/0	
	0.0	1 19	. 114	1.004	140	
UA12		1.14	114		114	
		1.00	114	7 500	£0 000	
UUS_2		0.37	84 89	7.009	82,449 82,220	
$\cup 1\Gamma_2$		0.55	84	1.490	84,449	

^a E. A. Wood suggested the preparation of this compound and correctly predicted that it would have the C15-type structure.

in Cu or Au. Copper, Ag, and Au nominally contribute one electron/atom when the d band is full.

The superconductivity and crystal-structure data

for C16-type compounds are given in Table XVII (references 82, 140, 149, 168, and 233–237).

C32, AlB_2 type, hexagonal. The only known superconductor with this type structure is β -ThSi₂. The data for C32 compounds are given in Table XVIII (references 82, 114, 149, 168, 171, 233, and 238-240).

TABLE XVI. Superconductivity and crystal-structure data for compounds with $C15_b$ -type structure.

	Super	conduc	tivity data	Crystal-structure data		
Compound	<i>T</i> ₅ °K	$^{T_n}_{^{\circ}\mathrm{K}}$	References	Lattice constants $a, Å$	References	
$PdBe_5$ $AuBe_5$ UCu_5		$0.35 \\ 1.02 \\ 1.02$	82 82 82	$5.995 \\ 6.097 \\ 7.037$	82,230 82,230,231 82,232	

C36, MgNi₂ type, hexagonal (Laves Phase). HfMo₂ is not superconducting above 1.02°K.¹¹³

C49, $ZrSi_2$ type, orthorhombic. The C49-type compounds investigated for superconducting properties include ZrSi₂ and ZrGe₂. ZrSi₂ is not superconducting

TABLE XVII. Superconductivity and crystal-structure data for compounds with $\dot{C}16$ -type structure.

			L	attice (Constan	ts
Com- pound	°K	$^{T_n}_{^{\circ}\mathrm{K}}$	References	a,Å	c,Å	References
BCr ₂		1.20	149			149
BMo_2	4.74		168,234			168,234
BW_2	3.10		149			149
$AlTh_2$		0.35	82	7.614ª	5.857ª	82,233
$MnSn_2$		1.12	234			234
FeGe ₂		1.02	82	5.911ª	4.951^{a}	82,235
$CoSn_2$		1.02;1.12	82;234	6.361ª	5.452^{a}	82,236
$CuAl_2$		1.02; 1.066	$5\ 82;234$	6.066ª	4.874^{a}	82,237
$CuTh_2$	3.49	,	140	7.28	5.75	140
$RhPb_2$	2.66		234			234
$PdPb_2$	2.95		234			234
$AgIn_2$	2.30 - 2.4	46	234			234
$AgTh_2$	2.26		140	7.56	5.84	140
AuPb ₂	4.42		234			234
$AuTh_2$	3.08		140	7.42	5.95	140

^a Powder patterns in present investigation were indexed based on these reported lattice constants.

above 1.02°K and ZrGe₂ is not superconducting above 0.35°K.82

²³³ J. R. Murray, J. Inst. Metals 84, 91 (1955–1956).
 ²³⁴ M. F. Gendron and R. E. Jones, J. Phys. Chem. Solids
 23, 405 (1962); Bull. Am. Phys. Soc. 6, 122 (1961).
 ²³⁵ H. J. Wallbaum, Z. Metallk. 35, 218 (1943).
 ²³⁶ O. Nial, Z. Anorg. Allgem. Chem. 238, 287 (1938).
 ²³⁷ A. J. Bradley and P. Jones, J. Inst. Metals 51, 131 (1933).
 ²³⁸ F. Larce. Naturnissensehaften 31, 145 (1943).

- ²³⁸ F. Laves, Naturwissenschaften **31**, 145 (1943).

²³⁹ I. P. Mayer, E. Banks, and B. Post, J. Phys. Chem. 66, 693 (1962)

²⁴⁰ C. P. Kempter and R. J. Fries, J. Chem. Phys. 34, 1994 (1961).

5

C54, $TiSi_2$ type, orthorhombic. TiGe₂ is not superconducting above 1.20°K.149

18

 C_{\circ} , ThSi₂ type, body-centered tetragonal. The data for compounds with this type structure are given in Table XIX (references 82, 149, 241, 242). To date

TABLE XVIII. Superconductivity and crystal-structure data for compounds with C32-type structure.

Com- pound	Super	conduc	tivity data	Crystal-structure data			
	°K	$^{T_n}_{^{\circ}\mathrm{K}}$	References	Lattice a,Å	constan c,Å	nts References	
$\begin{array}{c} CaGa_2 \\ TiB_2 \\ TiU_2 \\ VG \end{array}$		$1.02 \\ 1.28 \\ 1.06 \\ 0.05$		4.323ª	4.323ª	82,238 168 114 02,020	
${}^{1}Sl_{2}$ ZrB_{2} NbB_{2} TaB_{2}		$ \begin{array}{r} 0.35 \\ 1.8 \\ 1.28 \\ 1.28 \end{array} $	$82 \\ 171 \\ 168 \\ 168 $	3.85 ^a	4.14 ^a	$82,239 \\ 171 \\ 168 \\ 168 \\ 168$	
$\begin{array}{c} \operatorname{OsB}_2^- \\ \operatorname{ThAl}_2 \\ \beta - \operatorname{ThSi}_2 \end{array}$	2.41	$\begin{array}{c} 1.02\\ 0.35\end{array}$		2.876^{a} 4.388^{a}	2.871ª 4.162ª	$\begin{array}{c} 82,240 \\ 82,233 \\ 149 \end{array}$	

^a Powder patterns in present investigation were indexed based on these reported lattice constants.

only two superconductors have been reported, YGe₂ and α -ThSi₂.

DO₃, BiF₃ type, face-centered cubic. Alekseevskii, Brandt, and Kostina¹³⁰ report that BiLi₃ is normal down to 1.43°K. The reported lattice for the compound is 6.708 Å.130

TABLE XIX. Superconductivity and crystal-structure data for compounds with $C_{e^{-}}$ type structure.

Com- pound	Supe	rconducti	vity data	Crystal-structure data		
	^T [€] K	$^{T_n}_{^{\circ}\mathrm{K}}$	References	Lattice a,Å	e constai c,Å	nts References
$\begin{array}{c} & \text{YGe}_2 \\ \text{LaSi}_2 \\ \text{CeSi}_2 \\ \text{NdSi}_2 \\ \alpha\text{-ThSi}_2 \end{array}$	3.8 3.16	1.20;1.00 1.20;1.00 1.00	$\begin{array}{c} 241 \\ 149;241 \\ 149;241 \\ 241 \\ 149 \end{array}$			$\begin{array}{r} 241 \\ 149;241 \\ 149;241 \\ 241 \\ 149 \end{array}$
USi_2		0.35	82	3.98ª	13.74^{a}	82,242

^a Powder patterns in present investigation were indexed based on these reported lattice constants.

 DO_{18} , Na₃As type, hexagonal. The data for DO_{18} type compounds are given in Table XX (references 82, 130, and 243). No superconductors have been reported.

DO₁₉, Ni₃Sn type, hexagonal. The data for DO₁₉-

type compounds are given in Table XXI (references 82, 233, 244, and 245). The only superconducting compound is Al₃Th which has a transition temperature of 0.75°K.

TABLE XX. Superconductivity and crystal-structure data for compounds with DO18-type structure.

Com- pound	Superc	onduc	tivity data	Crystal-structure data		
	T _c °K	$^{T_n}_{^{\circ}\mathrm{K}}$	References	Lattice <i>a</i> ,Å	constant <i>c</i> ,Å	s References
Na₃Bi Si₃Ir α-K₃Bi		$1.39 \\ 1.02 \\ 1.40$	$130 \\ 82 \\ 130$	5.448 4.350ª 6.178	9.655 6.630ª 10.933	$130 \\ 82,243 \\ 130$

^a Powder patterns in present investigation were indexed based on these reported lattice constants.

DO₂₂, TiAl₃ type, tetragonal. No superconductors have been reported with this type structure. The data for the compounds investigated are given in Table XXII (references 82, 246, and 247).

TABLE XXI. Superconductivity and crystal-structure data for compounds with DO₁₉-type structure.

Com- pound	Super	conduc	tivity data	Crystal-structure data		
	<i>T₅</i> °K	$^{T_n}_{^{\circ}\mathrm{K}}$	References	Lattice a,Å	constant <i>c</i> ,Å	s Referen ces
Al₃Th Ti₃Ga Ti₃Sn	0.75	$0.35 \\ 1.02$	82 82 82	6.500ª 5.76ª 5.916ª	4.626^{a} 4.64^{a} 4.764^{a}	82,233 82,244 82,245

^a Powder patterns in present investigation were indexed based on these reported lattice constants.

TABLE XXII. Superconductivity and crystal-structure data for compounds with DO₂₂-type structure.

Com- bound	Superc	eonduc	etivity data	Crystal-structure data		
	$^{T_c}_{^{\circ}\mathrm{K}}$	$^{T_n}_{^{\circ}\mathrm{K}}$	References	Lattice a,Å	constant <i>c</i> ,Å	s References
ΓiAl₃ ΓiGa₃ ZrGa₃		$1.02 \\ 1.02 \\ 1.02$	82 82 82	5.436ª 5.558ª 5.616ª	8.596ª 8.109ª 8.730ª	$\begin{array}{r} 82,246\\ 82,247\\ 82,247\\ 82,247\end{array}$

^a Powder patterns in present investigation were indexed based on these reported lattice constants.

 DO_{23} , $ZrAl_3$ type, body-centered tetragonal. $ZrAl_3$ is not superconducting above 1.02°K.82

²⁴⁴ K. Anderko and U. Zwicker, Naturwissenschaften 44, 510 (1957).

- P. Pietrokowsky, J. Metals 4, 211 (1952).
 G. Brauer, Z. Anorg. Allegem. Chem. 242, 1 (1939).
 H. J. Wallbaum, Z. Metallk. 34, 118 (1942).

²⁴¹ B. T. Matthias, E. Corenzwit, and W. H. Zachariasen, Phys. Rev. 112, 89 (1958). ²⁴² W. H. Zachariasen, Acta Cryst. 2, 94 (1949).

²⁴³ L. N. Finnie, J. Less-Common Metals 4, 24 (1962).

 DO_{\bullet} , $Ni_{3}P$ type, body-centered tetragonal. Mo₃P has a transition temperature of 7.0°K.¹⁸⁵

 $D1_3$, $BaAl_4$ type, body-centered tetragonal. CaAl₄ is not superconducting above 1.02°K.82

D1_c, PtSn₄ type, orthorhombic. Recently Gendron and Jones²³⁴ investigated the occurrence of superconductivity in D1_c-type compounds and reported that PtPb₄ and AuSn₄ are superconducting at 2.80 and 2.38°K, respectively. PdSn₄ and PtSn₄ are not superconducting above 1.30°K.

 $D2_{c}$, $U_{6}Mn$ type, body-centered tetragonal. The superconducting properties of D2_c-type U compounds with Mn, Fe, Co, and Ni were investigated by Chandrasekhar and Hulm.¹¹⁴ The transition temperature of U₆Mn is 2.32°K, of U₆Fe, 3.86°K, of U₆Co, 2.29°K and U₆Ni is not superconducting above 1.12°K.

 $D5_2$, La_2O_3 type, trigonal. The compound α -Bi₂Mg₃ is not superconducting above 1.5°K.¹³⁰ The lattice constants for the compound are a = 4.666 Å and c = 7.401 Å.

D58, Sb2S3 type, orthorhombic. Alekseevskii, Brandt, and Kostina¹³⁰ report that Bi₂S₃ is not superconducting above 1.3°K. The lattice constants are a = 11.13Å, b = 11.27 Å and c = 3.97 Å.

 $D\gamma_b$, Ta_3B_4 type, orthorhombic. Nb₃B₄ and Ta₃B₄ are not superconducting above 1.28°K.¹⁶⁸

 $D8_8$, Mn_5Si_3 type, hexagonal. The data for $D8_8$ compounds are given in Table XXIII (references 82,

TABLE XXIII. Superconductivity and crystal-structure data for compounds with $D8_8$ -type structure.

Com- pound	Superc	onduc	etivity data	Crystal-structure data		
	°K	$^{T_n}_{^{\circ}\mathrm{K}}$	References	Lattice a,Å	constant <i>c</i> ,Å	s References
Ti ₅ Ge ₃		1.20	149			149
V ₅ Si ₃ ^b		0.35	82	7.135ª	4.842^{a}	82,248
V5Ge3b		1.02	82	7.295ª	4.970^{a}	82,249
Zr5Ge3		0.35	82	7.993ª	5.597ª	82,250
Zr5Pb3	4.60		82	8.529^{a}	5.864^{a}	82,251
$\mathrm{Nb}_5\mathrm{Si}_3{}^\mathrm{b}$		1.02	82	7.536^{a}	5.249^{a}	82,248

^a Powder patterns in present investigation were indexed based on these reported lattice constants. ^b Stabilized by the addition of 5 at. % C to the melt.

149, and 248–251). The only superconductor is Zr₅Pb₃ which has a transition temperature of 4.60°K.

 $D8_b$, CrFe type, tetragonal (Sigma phase). This structure seems to be favorable for the occurrence of superconductivity. Blaugher and Hulm¹⁴³ and Bucher, Heiniger and Müller¹⁴¹ have plotted the transition

TABLE XXIV. Superconductivity and crystal-structure data for compounds with D8_b-type structure.

	Supercond	luctiv	ity data	Crystal-structure data			
	T.	T_{r}	Ref-	Lattice of	eonstan	ts	
Compound	°ٌK	°ٌK	erences	a,Å	c,Å	References	
Cr₂Ru	2.0		111			111	
CrRe		1.02	82	9.20	4.78	82,153	
MnRe		1.02	82	9.23	4.79	82,252	
Zr ₃ Au		1.02	82	10.58	5.53	82	
Nb-Al	7.0 - 12.0		156			156	
Nbo 60Rho	4.04		141	9.80	5.07	141	
Nb-Rh	4.1		143			143	
Nb-Pd	2.0		143			143	
NbRe	2.0 - 3.8		141	9.79	5.10	141	
Nb-Re	2.0		143			143	
Nb2O82	1.78		140	9.844	5.056	140	
Nb ₂ Os ₂	1.85		141	9.85	5.06	141	
Nb-Os	1.4		143	0.00	0.00	143	
Nbo estro as	2.40		141	9.86	5.06	141	
Nho Iro	9.8		140	9.834	5.052	140	
Nb-Ir	7.9		143	0.001	0.00-	143	
Nhe Pto	3.73		140	9.91	5.12	140	
Nho en Pto a	• 4 01		141	9.91	5.13	141	
Nb-Pt	24		143	0.01	0.10	143	
MonaRun	$\frac{7.1}{7.0}$		141	9.55	4 95	141	
Mo_R11	40 1.0 6.0		143	0.00	1.00	143	
Mos roBes	-0.5		141	9.61	4 98	141	
Mos is Ros	801.070.1		141	9.59	4 07	141	
$M_{0.42}$	58 0.4		1/1	9.59	4.97	141	
Mo Do	65 8.0 60		1/2	5.01	1.91	1/12	
Mor Oa.	5.65		140	0.60	4 03	140	
$M_{0.62}O_{80.3}$	38 0.00		141	9.00	4.90	141	
Mo In	0.2		240	0.621	4 056	95 99 169	
Mo Tr	0.8		141	9.031	4.900	20,62,102	
$\Gamma_{0.7410.2}$	6 0.7	1.09	00	9.03	5 10	Q0 052 054	
r_{a} r_{b}	9.25	1.04	141	9.97	5.19	141	
$1 a_{0.60} \pi_{0.4}$	10 2.50		141	9.80	0.09	141	
r_{a}	2.0		140	0.77	F 00	140	
$1a_{0.40}$ $Re_{0.6}$	1.4		141	9.77	0.09	141	
1a-re	1.5	1.0	140	0.00	F 14	140	
$1a_{0.70}$ US0.3	0	1.4	141	9.00	0.14	141	
ra-Os		1.0	143	0.00	r 00	140	
$1 a_{0.651} r_{0.35}$		1.4	141	9.80	0.09	141	
ra-ir		1.0	143	10.09	F 90	145	
$ra_{0.80}$ Pt _{0.2}	(1.45)	1.2	141	10.02	5.20	141	
ra _{0.70} Pt _{0.3}	$\left\{ \hat{1}, \hat{5} \right\}^{-1}$	<1.2	141	9.93	5.16	141	
Ta-Pt	1.0	19	$143 \\ 141$			$143 \\ 141$	
$1a_{0.67}Au_{0.8}$	33	1.2	141	0.57	4.06	141	
W 0.60 KU0.4 W-R11	0 4.07 5.2		141	9.07	4.90	141	
Wo roBeo r	5.03		141	9.63	5.01	141	
W-Re	5 2		143	0.00	0.01	143	
$W_0 \approx 0 \approx 2$	25		113			113	
$W_{0.86}O_{S0.20}$	3.81		141	9.63	4.98	141	
Wo ex Oso av	38		113	0.00	2.00	113	
W_{-08}	44		143			143	
Wo zalro an	4 46		141	9.67	5.00	141	
110.72110.28	7.10		1.11	0.01	0.00	T T T	

temperatures against the average number of valence electrons per atom for σ -type phases and for α -Mn type (A12) phases of transition metal compounds. The maximum in the transition temperature occurs at about 6.5 valence electrons in the former's and at

²⁴⁸ H. Schachner, E. Cerwenka, and H. Nowotny, Monatsh. Chem. 85, 245 (1954). ²⁴⁹ E. I. Gladyshevskii and Yu. B. Kuz'ma, Dopovidi Akad.

Nauk Ukr. RSR 1958, 1208; Chemical Abstracts 53, 9010 (1959).

²⁵⁰ É. Parthé and J. T. Norton, Acta Cryst. 11, 14 (1958). ²⁵¹ H. Nowotny and H. Schachner, Monatsh. Chem. 84, 169 (1953).

6.65 in the latter's plot. These values are in agreement with the empirical rules derived for the occurrence of superconductivity and the criteria for the maximum transition temperature.

TABLE XXV. Superconductivity and crystal-structure data for compounds with D10₂-type structure.

	Supercor	iductiv	vity data	Crystal-structure data				
Compoun	d °Ḱ	$^{T_n}_{^{\circ}\mathrm{K}}$	Ref- erences	Lattice <i>a</i> ,Å	constant c,Å	s References		
Ru7B3	2.58		140	7.465	4.715	140		
Rh_7B_3		0.35	82	7.47	4.78	82,255		
Th7Fe3	1.86		140	9.823	6.211	140		
Th7Co3	1.83		140	9.833	6.200	140		
Th7Ni3	1.98		140	9.885	6.225	140		
Th_7Rh_3	2.15		82	10.031ª	6.287^{a}	82,256		
Th ₇ Os ₃	1.51		140	10.02	6.285	140		
Th7Ir3	1.52		140	10.06	6.290	140		
$\mathrm{Th_7Pt_3}$		1.02	82	10.126ª	6.346ª	82,256		

* Powder patterns in present investigation were indexed based on these reported lattice constants.

The superconductivity and crystal-structure data are given in Table XXIV (references 25, 82, 111, 113, 140, 141, 143, 153, 156, 162, and 252–254).

 $D8_i, Mo_2B_5$ type, rhombohedral. Mo_2B_5 is not superconducting above 1.28°K.¹⁶⁸

D102, Th7Fe3, hexagonal. Superconductivity has been observed in several compounds with this type structure. The data are given in Table XXV (references 82, 140, 255, 256).

E93, Fe3W3C type, face-centered cubic. The superconducting properties of some recently reported Ti₂Ni type phases (isomorphous with Fe₃W₃C type) are given in Table XXVI (references 82, 140, 257, and 258). This is the only structure known in which the presence of oxygen, required for the stabilization of some of these compounds, is not detrimental to the superconducting behavior.

 $L1_0$, CuAu type, tetragonal. The compounds α -LiBi and NaBi crystallize in this structure and are superconducting at 2.47°K¹³⁰ and 2.25°K,¹⁷⁴ respectively. The reported lattice constants for α -LiBi are a = 3.361 Å and c = 4.247 Å¹³⁰ and for NaBi, a = 3.46Å and c = 4.80 Å.^{130,132}

²⁵² E. M. Savitskii, M. A. Tylkina, et al., Russ J. Inorg. Chem. 6, 755 (1961).
 ²⁵³ K. P. Gupta, Trans. AIME 221, 1047 (1961).
 ²⁵⁴ H. Nowotny, C. Brukl, and F. Benesovsky, Monatsh.

Chem. 92, 116 (1961). ²⁵⁵ B. Aronsson, E. Stenberg, and J. Åselius, Acta Chem.

- ²⁵⁶ J. R. Thomson, Nature 189, 217 (1961).
 ²⁵⁷ M. V. Nevitt, J. W. Downey, and R. A. Morris, Trans.
 AIME 218, 1019 (1960).
 ²⁵⁸ N. Karlsson, quoted in K. Kuo, Acta Met. 1, 301 (1953).

 $L1_2$, Cu_3Au type, cubic. The data for $L1_2$ compounds that have been investigated for superconductivity are given in Table XXVII (references 82, 140, 168, 216, and 259-264). The superconductors are SrBi₃, Zr₃Al, and La₃In.

TABLE XXVI. Superconductivity and crystal-structure data for compounds with $E9_3$ -type structure.

	Super	condi data	uctivity i	Crystal-structure data			
Compound	<i>T</i> . °K	$^{T_n}_{^{\circ}\mathrm{K}}$	Ref- erences	Lattice constants <i>a</i> ,Å	References		
Γi₂Co	3.44		140	11.30	140		
Ti0.573Cu0.287O0.14		1.02	82	11.446	82.257		
Ti0.573Rh0.287O0.14	3.37		82	11.588	82.257		
Ti0.573Ir0.287O0.14	5.5		82	11.620	82,257		
Zr ₃ V ₃ O	7.5		82	12.160	82,258		
Zr0.61Rh0.285O0.105	11.8		82	12.408	82,257		
Zr _{0,61} Pd _{0,285} O _{0,105}	2.09		82	12.470	82,257		
Zr _{0.65} Ir _{0.265} O _{0.085}	2.30		82	12.430	82,257		
Hf_2Fe		0.35	82	12.043 - 12.06	$5\ 82,257$		
Hf_2Co		0.56	82	12.067	82,257		
Hf _{0.67} Ni _{0.233} Ru _{0.10}		1.02	82	12.183	82,257		
${ m Hf_{0.63}Ni_{0.25}Re_{0.12}}$		1.02	82	12.173	82,257		

 L'_{2b} , ThH_2 type, body-centered tetragonal. ZrH_2 which crystallizes in the L'_{2b} -type structure is not superconducting above 1.02°K.37,82

 L'_3 , W_2C type, hexagonal. Mo₂C, Ta₂C, and W₂C have been reported superconducting at 2.78,¹⁶⁸

TABLE XXVII. Superconductivity and crystal-structure data for compounds with L_{12}^{-} -type structure

Compound	Super	conduc	tivity data	Crystal-structure data		
	<i>T</i> ^c °K	$^{T_n}_{^{\circ}\mathrm{K}}$	References	Lattice constants a, Å	References	
VZn ₃	, as red table	1.02	82	3.846	82	
$SrBi_3$	5.62		168	5.042	216	
Zr ₃ Al	0.73		82	4.37	82,259	
Zr ₃ In		1.02	82	4.46	82.260.261	
NbZn ₃		1.02	82	3.932	82,262	
La ₃ In	10.4		140	5.07	140	
LaIn ₃		1.02	82	4.734	82,263	
UGe3		0.35	82	4.206	82,264	

²⁵⁹ J. H. Keeler and J. H. Mallery, J. Metals 7, 394 (1955). ²⁶⁰ K. Schubert, H. G. Meissner, M. Pötzchke, et al., Naturwissenschaften 49, 57 (1962).
 ²⁶¹ J. O. Betterton, Jr. and W. K. Noyce, Trans. AIME.

212, 340 (1958)

 ²⁶² C. L. Vold, Acta Cryst. 13, 743 (1960).
 ²⁶³ A. Iandelli, "Intermetallic Compounds of the Rare Earth Metals," *Proceedings of Symposium on Physics, Chemistry of*. Metals," Proceedings of Symposium on Physics, Chemistry of Metallic Solutions and Intermetallic Compounds (Chemical Publishing Company, New York, 1960), Paper No. 3F. ²⁶⁴ B. R. T. Frost and J. T. Maskrey, J. Inst. Metals 82,

171(1953)

3.26,^{149,265} and 2.74°K,¹⁶⁸ respectively. However, recently Giorgi and Szklarz²⁶⁶ report that Ta₂C is not superconducting down to 2.0°K, and in our opinion this is the more reliable value.

Cubic compounds. The superconductivity and crystal-structure data for various cubic compounds which have been investigated are given in Table XXVIII (references 82, 114, 168, 171, 174, 191, 265, and 267-277).

TABLE XXVIII. Superconductivity and crystal-structure data for cubic compounds.

. 1	Supercon	ductiv	vity data	Crystal-structure data			
Compound	<i>T</i> d °K	${}^{T_n}_{ m \circ K}$	Ref- erences	$\begin{array}{c} \text{Lattice} \\ \text{constants} \\ a, \text{\AA} \end{array}$	Lattic type ^a	e References	
Mg_2Al_3	0.84		82	28.28	fee	82,267	
TiH_2		1.02	82	4.444	fee	37,82	
CrGa ₄		1.02	82	5.648	\mathbf{bec}	82,268	
$Cu_{1.8}S$		1.3	191		\mathbf{fec}	191	
Cu ₁₈ As ₄ Sl	Q3	0.35	82	7.540	р	82,269	
Mo_2N	5.0		168		fcc	168	
$MoAl_{12}$		1.02	82	7.580	bcc	82,270,271	
$\mathrm{Pd_{17}Se_{15}}$		1.00	272	10.606	р	273	
Cs_3Bi		b	174	9.305	\mathbf{fcc}	174	
$LaH_{2.45}$		1.8	171	5.636	\mathbf{fcc}	171	
$LaCd_{11}$		0.35	82	9.331	р	82,274	
W_2C	5.2		265	4.25	\mathbf{fcc}	265	
W_2N		1.28	168		\mathbf{fcc}	168	
$\mathrm{ReN}_{0.34}$	4.0		275		\mathbf{fcc}	275	
AuZn ₃	1.21		82	7.893	р	82,269	
α -Bi ₄ Rh		0.10	276	14.928	\mathbf{bcc}	277	
UCo	1.70		114		bcc	114	

^a fcc-face-centered cubic; bcc-body-centered cubic; p-primitive. ^b Not stated.

Tetragonal compounds. The superconductivity and crystal-structure data for tetragonal compounds are given in Table XXIX (references 82, 114, 132, 133, 149, 165, 168, 216, and 278 to 284). Rögener¹⁶⁵ determined the transition temperature of the face-cen-

- ²⁶⁵ G. Lautz and D. Schneider, Z. Naturforsch. 16A, 1368
- (1961). ²⁶⁶ A. L. Giorgi and E. G. Szklarz, Bull. Am. Phys. Soc. 7, 176 (1962). ²⁶⁷ H. Perlitz, Trans. Chalmers Univ. Technol., Gothenberg
- 50, 3 (1946).
 ²⁶⁸ K. Schubert, T. R. Anantharaman, et al., Naturwissenschaften 47, 512 (1960).
 ²⁶⁹ K. Schubert, H. Breimer, et al., Naturwissenschaften
- ²⁶⁹ K. Schubert, H. Breimer, *et al.*, Naturwissenschaften **44**, 229 (1957).
- ²⁷⁰ J. Adam and J. B. Rich, Acta Cryst. 7, 813 (1954).
 ²⁷¹ J. W. H. Clare, J. Inst. Metals 89, 232 (1961).
 ²⁷² B. T. Matthias and S. Geller, J. Phys. Chem. Solids 4,
- 318 (1958) S. Geller, Acta Cryst. 15, 713 (1962).
- ²⁷⁴ A. Iandelli and R. Ferro, Gazz. Chim. Ital. 84, 463 (1954).
 ²⁷⁵ B. T. Matthias and W. H. Zachariasen, J. Phys. Chem. Solids 7, 98 (1958).
 ²⁷⁶ N. E. Alekseevskii, G. S. Zhdanov, and N. N. Zhuravlev,
- Soviet Phys.-JETP 1, 99 (1955). ²⁷⁷ V. P. Glagoleva and G. S. Zhdanov, Soviet Phys.-JETP
- 3, 155 (1956).

tered tetragonal Nb-N compounds as a function of composition and found that the maximum transition temperature, 11.8°K, occurred in NbN_{0.79}. Lautz and Schröder²⁷⁸ reported that NbN_{0.8} had a transition

TABLE XXIX. Superconductivity and crystal-structure data for tetragonal compounds

	Superconductivity data			Crystal-structure data					
Com- pound	<i>T</i> °K	$^{T_n}_{^{\circ}\mathrm{K}}$	Ref- erences	a,Å	Lattice constants <i>c</i> ,Å	Lat- tice type ^a	References		
V ₅ Si ₃		0.30	82	9.429^{b}	4.757 ^b	be	82,279		
Cr ₃ Ge ₂		1.20	149			be	149		
CuGa ₂		1.27	82	2.836^{b}	5.847^{b}	p	82.280		
Nb-N	-8.90	/11.8	165.278			fe	165.278		
Nb ₅ Si ₃		1.02	82	10.018^{b}	5.072^{b}	\mathbf{bc}	82.279		
Nb ₅ Ge	3	1.02	82	10.148^{b}	5.152^{b}	$\mathbf{b}\mathbf{c}$	82,281		
Nb_3Sn_2	16.6		с	6.90	9.53		ć		
RhIn ₃		1.02	82	7.01^{b}	7.15^{b}	p	82,282		
β-PdBi	$_{2}$ 4.25		133	3.362	12.983	ĥс	132,133		
BaBi ₃	5.69		168	5.188	5.157		216		
HgCd	1.77		82	3.940^{b}	2.916^{b}	\mathbf{bc}	82,283,284		
$T\bar{h}_3Si_2$		1.20	149			р	149		
U ₃ Si		1.10	114			bе	114		

^a bc-body-centered; fc-face-centered; p-primitive. ^b Powder patterns in present investigation were indexed based on these reported lattice constants. ^c Note added in proof. T. B. Reed and H. C. Gatos, J. Appl. Phys. 33, 2657 (1962).

temperature of 8.9°K. Hardly and Hulm¹⁴⁹ found that Nb₄N₃ was superconducting at 7.2°K and Schröder¹⁶⁶ reported that face-centered tetragonal Nb $(N + 0)_{0.77}$ had a transition temperature of 6.80°K.

Hexagonal compounds. The data for hexagonal compounds are given in Table XXX (references 149, 166, 168, 174, 190, 266, 276, 285, and 286).

Orthorhombic compounds. The superconductivity and crystal-structure data for orthorhombic compounds are given in Table XXXI (references 82, 108, 130, 131, 133, 134, 149, 196, 197, 241, 276, and 287-290).

- ²⁷⁸ G. Lautz and E. Schröder, Z. Naturforsch. 11A, 517 (1956).
- 279 E. Parthé, H. Nowotny, and H. Schmid, Monatsh. Chem. 86, 385 (1955)
- ²⁸⁰ E. Zintl and O. Treusch, Z. phys. Chem. **34B**, 225 (1936). ²⁸¹ H. Nowotny, A. W. Searcy, and J. E. Orr, J. Phys. Chem.
- 60, 677 (1956).
 ²⁸² K. Schubert, H. L. Lukas, H. G. Meissner, and S. Bhan,
- ²⁶⁵ K. Schubert, H. L. Lukas, H. G. Meissner, and S. Bhan,
 Z. Metallk. 50, 534 (1959).
 ²⁸³ R. F. Mehl, J. Am. Chem. Soc. 50, 381 (1928).
 ²⁸⁴ K. Schubert, U. Rösler, *et al.*, Z. Metallk. 45, 643 (1954).
 ²⁸⁵ N. N. Zhuravlev and G. S. Zhdanov, Izvest. Akad. Nauk SSSR, Ser. Fiz. 20, 708 (1956).
- ²⁸⁶ N. E. Alekseevskii and Yu. P. Gaidukov, Zh. Eksp. i Teoret. Fiz. 25, 383 (1953)
- ²⁸⁷ K. Schubert and H. Pfisterer, Z. Metallk. 41, 433 (1950). ²⁸⁸ V. P. Glagoleva and G. S. Zhdanov, Zh. Eksp. i Teoret.
- Fiz. 26, 337 (1954) ²⁸⁹ R. N. Kuz'min and G. S. Zhdanov, Soviet Phys.-Cryst. 5, 830 (1961). ²⁹⁰ B. A. Hatt, Acta Cryst. 14, 119 (1961).

	Super	rconductiv	vity data	Crystal-structure data			
Com- pound	<i>T</i> . °K	${}^{T_n}_{^{\circ}\mathrm{K}}$	Ref- erences	Lattice o a,Å	constants c,Å	Ref- erences	
$\overline{V_2C}$ V ₅ N ₂		$1.20 \\ 1.20$	$149 \\ 149$	2.944	4.608	$149 \\ 149$	
$Nb_2\tilde{C}$	9.18	2.0ª	$\frac{149}{266}$	3.105	4.970	$\frac{149}{266}$	
Nb₂N MoN Ta₂N	12.0	1.20;1.94	$149;166 \\ 168 \\ 149$	3.050	4.954	166 168 149	
γ -Bi ₄ Rh BiIn ₂	$2.7 \\ 5.6 \\ 0.155$	1.20	$276 \\ 190 \\ 202$	0.44	6 9F	285 190 174	
β -B1 ₂ Pt	0.155		286	6.44	6.25	174	

TABLE	XXX.	Superconductivity	and	crystal-structure	data
		for hexagonal co	mpo	unds.	

TABLE	XXXI.	Superconductivity and crystal-structure	
	data	for orthorhombic compounds.	

Superconductivity

data				Crystal-structure data				
Com- pound	<i>Т.</i> °К	$^{T_n}_{^{\circ}\mathrm{K}}$	Ref- erences	Latt a,Å	ice const <i>b</i> ,Å	cants c,Å	Ref- erences	
$\begin{array}{c} \text{CoGe}_3 \\ \text{NiBi}_3 \\ \text{Ge}_3 \text{Rh}_5 \\ \text{YSi}_2 \\ \text{Rh}_2 \text{B} \\ \text{LaGe}_2 \\ \beta \text{-Bi}_3 \text{Rh} \\ \text{BiPd} \\ \text{URe}_2 \end{array}$	$\begin{array}{c} 4.06 \\ 2.12 \\ 1.49 \\ 3.2 \\ 3.7 \end{array}$	0.35 1.0 1.0	$\begin{array}{r} 82\\ 130\\ 108\\ 149,241\\ 196\\ 241\\ 276\\ 131,133\\ 82\\ \end{array}$	5.66 ^a 8.875 5.42 9.027 7.203 5.600 ^a	5.66^{a} 4.112 10.32 4.24 8.707 9.178^{a}	10.82^{a} 11.477 3.96 11.522 10.662 8.463	82,287 288 197 241 197 241 289 134 * 82,290	

* In our opinion this is a more reliable value.

^a Powder patterns in present investigation were indexed based on these reported lattice constants.

TABLE XXXII. Superconductivity and crystal-structure data for monoclinic compounds.

	Supercon	ductiv	vity data	Crystal-structure data					
Compound	d °K	$^{T_n}_{^{\circ}\mathrm{K}}$	Ref- erences	a,Å	Lattice b,Å	constants c,Å	β	Ref- erences	
lpha-Bi ₂ Rh eta-Bi ₂ Rh lpha-Bi ₂ Pd	1.70–1.75	$1.34 \\ 1.27$	276,285 276 130-134	$6.96 \\ 16.2 \\ 12.74$	$6.83 \\ 7.0 \\ 4.25$	$7.01 \\ 10.5 \\ 5.665$	118.2° 92°30′ 102°35′	$291 \\ 292 \\ 133,134$	

Monoclinic compounds. The data for monoclinic compounds which have been investigated for superconducting properties are given in Table XXXII (references 130-134, 276, 285, 291, and 292).

Superconducting compounds of unknown crystal structure. Many superconducting compounds whose crystal structures were not specifically stated or were not determined have been reported. Data for these are given in Roberts' compilation.³¹

Recently we have found that Zr_3Sb_2 is superconducting at 1.74°K and Zr_{0.7}Bi_{0.3} at 1.51°K.⁸² The patterns for these substances have not been interpreted as yet. Raub and co-workers²⁹³ report that superconductivity occurs in the Pd-As system for alloys with the approximate composition of Pd₂As and also in alloys containing Co or Ni additions. The superconducting transition temperature of LaSi₂ begins at about 2.5°K.294 Previous measurements of tetragonal LaSi₂ (C_{e} type) indicated that the compound was not superconducting above 1.00°K.^{149,241}

1, 91 (1955). ²⁹³ C. T. Raub, G. W. Webb and R. W. Fitzgerald, Bull. Am.

However, the structure of the superconducting LaSi₂ compound is not stated. Szklarz and Giorgi¹⁷⁶ have recently reported superconductivity data for HfN and for HfN-ZrN solid solutions. The transition temperature for HfN is 6.2°K and for the solid solutions the transition temperatures range from 6.2 to 10.7°K. The structure of these phases was not stated but they are probably the cubic NaCl type (Bl). Compounds of Li, Na, or Pt with Hg have been reported superconducting.²⁹⁵ The transition temperature for Hg₃Li is 1.8°K; for Hg₄Na, 3.0°K; for Hg₂Na, 1.6°K; and for Hg₄Pt, 3.5°K. Note added in proof. W. E. Henry [Bull. Am. Phys. Soc. 7, 621 (1962)] reports that La₅Si₃ is superconducting at 1.6°K.

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²⁹¹ G. S. Zhdanov and R. N. Kuz'min, Soviet Phys.-Cryst. 6, 704 (1962). ²⁹² N. N. Zhuravlev and G. S. Zhdanov, Soviet Phys.-JETP

Phys. Soc. 7, 474 (1962). 294 W. E. Henry, C. Betz, and H. Muir, Bull. Am. Phys.

Soc. 7, 474 (1962).

²⁹⁵ M. F. Merriam, Bull. Am. Phys. Soc. 7, 474 (1962).