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ABSTRACT

In general there are actually two different types of A-15 compounds (A_3B) whose superconducting properties depend on whether the B atoms are transition elements (s-d type) or non-transition elements (s-p type). The properties in which the s-d type superconductors show marked differences in behavior from the s-p type include: 1. stoichiometry and range of composition, 2. the strong influence of N(0) on the stability and T_c of the phase, and 3, the effect of composition and atomic ordering on the T_c of the phase. These differences are discussed and a conclusion presented.

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PROPERTIES OF s-p AND s-d TYPE A-15
SUPERCONDUCTORS - A COMPLETION*

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The A-15 crystal structure, shown in Fig. 1, was discovered in 1931 (Hartman, et al, 1931) when an oxide of tungsten was mistaken for a polymorphic form of tungsten and the new phase called beta tungsten (β -W). Later when the error was discovered, crystallographers renamed the structure A-15 or Cr₃Si type. However, the name beta tungsten has persisted so that at present there are four designations which are used interchangeably: A-15, β -W, Cr₃Si and Cr₃O. Superconductivity was first observed in an A-15 phase in 1953 (Hardy and Taha, 1953) when it was found that V₃Si was superconducting with a transition temperature, T_c, of 17.1 K, a record high T_c at the time. Since then the record high T_c superconductors have consistently been A-15 phases and include Nb₃Ga at 18.4 K (Sathler, et al, 1954), Nb₃Al_{0.8}Ge_{0.2} at 20.4 K (Matthias et al, 1957), Nb₃Ga at 20.3 K (Webb et al, 1971) and Nb₃Ge at 23.2 K (Gavrilov et al, 1974; Testardi et al, 1974). At present there are over 70 intermetallic compounds with an A-15 structure and approximately 50 of these are superconducting.

The idealized composition for the A-15 phase is A₃B with the A atoms occurring in pairs on each of the faces of a cubic cell and forming three orthogonal lines or "chains" of atoms as illustrated in Fig. 1. The B atoms are arranged in a body-centered-cubic configuration. The interatomic distance between the A atoms in the chains is much closer than in the pure A metal crystal and the superior superconducting properties of this structure is believed associated with these chains.

The conditions considered favorable for the formation of the A-15 phase are:

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1. As shown in Fig. 2, the A-atoms are limited to the transition elements in groups 4A, 5A and 6A while the B-atoms can be either the transition elements in groups 7A through 10A or the nontransition elements in groups 1B through 5B.

2. The ratio of the Goldschmidt CN12 radii of the A and B atoms (r_A/r_B) should be within the limits of 0.94 and 1.12 with a value close to unity being the most favorable.

3. The valence electron per atom ratio (e/a) most favorable for the occurrence of the superconducting phase are 4.75 and 6.5 (Roberts, 1969) as shown in Fig. 3. These values are remarkably close to the values proposed by Matthias (1955) for the occurrence of high T_c in compounds. They also correspond to the maxima in the density of states at the Fermi level, $N(0)$, versus e/a curve as determined by Morin and Matla (1963).

It was originally believed that the A-15 phases were nicely ordered compounds with narrow composition ranges which occurred close to the ideal A_3B composition and always on the A-rich side. However, it was soon learned that this was not always true. Work by Waterstrat and van Reth (1966) on the Cr-Pt and Cr-Os systems showed not only were nonstoichiometric A-15 phases stable over an extended composition range but often the composition range did not even include the A_3B composition. Other investigators (Blaugher et al, 1969; Hartsough, 1974; and Flukiger et al, 1974) later pointed out that there are actually two different types of A-15 compounds whose superconducting properties depended on whether the B atoms were transition elements or nontransition elements. It has been suggested (Flukiger et al, 1974) that the two classes be designated as typical and atypical A-15 compounds to differentiate between the two types. A more reasonable classification would be one based on the electron characteristics of the B atoms. For the purpose of the present paper the two types of A-15 compounds will be distinguished as "s-p type" for the compounds with nontransition elements as B atoms, and "d type" for the compounds in which the B atom is a transition element. The various d type of A-15 compounds are shown in Fig. 4. A total of 26 binary compounds are represented including the recently discovered A-15 phase in the V-Re system (Glori et al, 1978). Superconductivity has been observed in 23 of the 26 d type A-15 compounds.

The superconducting properties in which the d type of A-15 superconductors show marked differences in behavior from the s-p type include:

- I. Stoichiometry and range of composition.
- II. The strong influence of the $N(0)$, as shown by the e/a ratio, on the stability and T_c of the A-15 phase.
- III. The effect of composition and atomic ordering on the T_c of the A-15 phase.

I. BACKGROUND AND STATE OF CURRENT KNOWLEDGE

An empirical correlation between the T_c and the range of composition (solid solution range, SSR) has been proposed (Gunn, 1974; Wang, 1977) which shows that in general the T_c of the superconducting A-B compounds is proportional to the range of composition of the phase. However, when this correlation is applied to all superconducting A-B materials, large variations are found for a number of compounds, e.g. V-Pt, V-Rh, Nb-Ti, etc., and these variations occur predominantly for the red type of A-B compounds. To study the T_c vs. T_c vs. T_c phase correlation, each cluster of correlation between T_c and the range of composition resulting is shown in Fig. 1. Further, for the red type, the range of composition occurs close to the ideal composition, A₁B₁, and extends in the direction of higher A atom content. The cluster of A atoms appears to be continuous with either formation of vacancies on the B sublattice, or the excess A atoms occupy positions on the A sublattice. The T_c in these systems is shown in Fig. 2, and the correlation between the stability and the A₁B₁ composition.

The red type A-B compounds, on the other hand, show wide variations in composition which can extend in either the A rich or the B rich direction. The range of composition has little relation to the T_c , and for phases with a composition range extending on both sides of the stoichiometric A₁B₁ composition, the maximum T_c does not occur at the A₁B₁ composition. In fact some of the red type of A-B phases exhibit high T_c near an off-stoichiometric composition which shows extreme variation from the ideal A₁B₁ atomic composition, e.g. V_{0.50}Pt_{0.50} with a T_c of 5.15 K (Blaugher et al., 1969); Mo_{0.4}Tc_{0.6} - T_c = 13.4 K (Darby and Zoller, 1962); and V_{0.4}Pt_{0.6} - T_c = 8.4 K (Gunn et al., 1977).

II. EFFECT OF c/a ON STABILITY AND T_c

According to Laves (1956) for the A-B structure to form, the Goldschmidt CN12 radius ratio of the constituent atoms must be close to unity. After an extensive examination of the various stable A-B phases, Laves later concluded (Bartnough, 1974) that this radius ratio must lie between 0.84 and 1.12. However, the size factor alone is not a sufficient condition for determining whether an A-B structure will form. Compounds such as Nb₃As and Nb₃P have favorable size factors but the phases do not form. Zn and Hf have almost identical radii, yet no A-B compounds of III exist. So another factor, namely the electron relationship of the component atoms, exerts a strong influence on the formation of these phases. This is shown in Fig. 3 by the large number of A-B compounds which have c/a

ratios close to 4.7 and 6.5. Since the s-p type A-15 compounds form at compositions close to the stoichiometric values, over a wider range of c/a ratios depending on the nature of the B atom. However, all of the compounds with high T_c values form at the favorable c/a ratios.

In the s-d type A-15 compounds the c/a ratio exerts a major influence and essentially dictates the composition, where the A-15 phase is most likely to form. Thus the s-d type A-15s form over a narrower range of c/a ratios and a much wider range of compositions. The higher T_c values again occur near the favorable c/a ratio of 6.5. This effect of the c/a ratio was first confirmed by changes in the T_c of Nb_3Al and Nb_3Ga induced in the phases Ga-Pb and Pb-Al by the addition of lead (Rault, 1966). A more dramatic example is shown in Fig. 6 which includes the variation of composition for the A-15 phases of compounds V-X , where $\text{X} = \text{Re}, \text{Os}, \text{Ir}, \text{Pt}$ and Au (Giangi et al., 1975). These compounds are found to vary from the ideal 1:1 atomic composition of $\text{V}_2\text{X}_{1.2}$ and $\text{V}_2\text{X}_{1.2}$ to the extreme atomic composition of $\text{V}_2\text{Re}_{0.71}$ in a continuous series. Even while the c/a ratio of all of these compounds is in the range 6.1 to 6.6, the T_c varies from 6.6 to 10.1 K.

III. EFFECT OF ATOMIC ORDERING

The effect of atomic ordering on the T_c of A-15 phases has been the subject of a number of investigations. The long range or long range crystallographic order (LRO) in A-15 phases was first suggested by Barak (Barak et al., 1965) to explain the variation of T_c for vapor deposited Nb_3Al . Van Beeth and Beneratrat (1968) using x-ray diffraction methods determined the Bragg-Williams long range order parameter S , for a number of A-15 compounds. They concluded that the s-p type of A-15 phases have compositions close to the stoichiometric Aq_2 and are highly ordered, while the s-d type A-15s have compositions off stoichiometry and are disordered. Blaugher et al., (1969) found that atomic ordering by low temperature anneals caused T_c to increase in a number of s-p type systems. They also found that for the s-d type A-15 phases in the Cr-Ge and V-Ge systems, the T_c increased when the compositions departed from stoichiometry. Similar increases in T_c by low temperature anneals have been found in $\text{Nb}_3\text{Al}_{1.8}\text{Ge}_{0.2}$ (Sullivan et al., 1967), Nb_3Ge (Gebb et al., 1971) and V_3Ga (Koch 1973). The most interesting ordering effect was observed in the V_3Au system (Gebb et al., 1971) where the A-15 phase occurs at the stoichiometric composition and has an extremely narrow range of homogeneity. The superconducting behavior was found to vary from non superconductivity above 6.015 K to a $T_c = 4.2$ K as the order parameter was increased by low temperature anneals.

A method that has proven very effective in producing relatively large amounts of disorder is by bombarding the sample with high energy neutrons ($E = 1.5 \text{ MeV}$) to a fluence (neutrons/cm²) of approximately 10^{19} . This method permits progressively amounts of disorder to be introduced to occur uniformly throughout the sample without any change in either the crystal structure or the stoichiometry. Using high energy neutron irradiation, Swedler et al, (1974, 1975) studied the effect of ordering on the T_c of the s-p type superconductors: Kb_3Sn , Nb_3Al , Nb_3Ga , Nb_3Ge and V_3Si . Depression in T_c from 18% to greater than 90% resulted as the fluence increased from 10^{18} to 10^{19} . A similar study was carried out by Swedler et al, (1977) on the s-p type Bi_2Se_3 (Gersdorfer et al, 1977) resulting in a similar depression in T_c (34 to 65%), and a more recent study on the irradiation of the A-15 phase $\text{Nb}_3\text{Ge}_{1-x}\text{Si}_x$ (Cox et al, 1979) resulted in an even smaller depression in T_c (0 to 3%). Of interest is the observation that similar depressions in T_c were observed when the disorder was effected by converting the A-15 structure to an A-2 (b.c.) structure at the same composition using ion bombardment techniques. Hughes et al, (1966) succeeded in converting the A-15 phase of Nb_3Sn to the A-2 structure and found the T_c decreased from 11.4 K to 9.6 K. A more recent study of this system (Stewart et al, 1977) showed that the drop in T_c was due to a corresponding drop in $K(0)$. Williams et al, (1966) converted Nb_3Al from the A-15 to the A-2 form with a depression in T_c from 13.0 K to 10.1 K. Recently Glini et al, (1973) succeeded in converting the light-disordered s-d type A-15 Nb_3Te from A-15 to A-2 and observed essentially no change in T_c . These results suggest that A-15 compounds will have the highest T_c values when they have the ideal stoichiometry and the A atoms form a totally unfrustrated monatomic system with only B atoms in the B sublattice. For an entirely disordered A-15 lattice, the superconducting behavior is both the s-p and the s-d type A-15, and therefore correspond to that of a bcc lattice with a comparable c/a ratio.

REFERENCES

- Blaugher, R. D., Pein, R. E., Cox, J. F., and Rutenfranz, J. V. (1969). J. Appl. Temp. Phys. 1, 579.
- Bucher, E., Laves, P., Muller, J., and van Philipborn, H. (1964). Phys. Letters 8, 27.
- Darby, J. B. and Ziegler, S. T. (1962). J. Phys. Chem. Solids. 23, 1825.
- Flukiger, R., Paoli, A., and Muller, J. (1974). Solid State Commun. 14, 443.
- Gavaler, J. R., Pein, R. E., and Blaugher, R. D. (1971). J. Appl. Phys. 42, 3407.
- Giorgi, A. L., Matthias, B. T., and Stewart, G. R. (1973). Solid State Commun. 21, 291.
- Giorgi, A. L. and Matthias, B. T. (1973). Phys. Rev. B7, 2360.
- Giorgi, A. L., Stewart, G. R., and Schuler, F. G. (1973). The Electrochemical Society Extended Abstracts, Boston Meeting, May 6-11, 1973, p. 403.
- Good, J. J., Cox, G. W., Allen, P. L., and Pein, R. E. (1963). "High Temperature Fields" (McGraw-Hill, New York).
- Hardy, G. F. and Deha, J. R. (1964). Phys. Rev. 137, 1884.
- Hartmann, H., Ebert, P., and Bredschneider, O. (1961). Z. Natur- und Angewandte Chem. 12, 116.
- Hartnough, L. D. (1964). J. Phys. Chem. Solids 15, 171.
- Hole, R. A., Cox, J. L., Blaugher, R. D., Koenigsberg, P. H., and van Renth, L. C. (1971). J. Chem. 55, 525.
- Koch, G. C. (1971). J. Phys. Chem. Solids 32, 1445.
- Matthias, B. T. (1955). Phys. Rev. 97, 74.
- Matthias, B. T., Geballe, T. H., Gellert, P., and Corcoran, L. (1954). Phys. Rev. 95, 1635.
- Matthias, B. T., Gellert, T. H., Lein, J. L., Hull, G. W., J. E., Hull, G. W., J., Williams, R. L., and Muller, J. P. (1967). Science 156, 645.
- Martin, F. J. and Hiltz, J. P. (1963). Phys. Rev. 129, 1115.
- Roberts, W. W. (1969). "Superconducting Materials" Ed. Technical Note 482.
- Stewart, G. R. and Giorgi, A. L. (1973). Solid State Commun. 20, 669.
- Szwedler, A. R., Schatzler, D. G., and Cable, G. M. (1971). Phys. Rev. Letters 33, 163.
- Szwedler, A. R. and Cox, J. F. (1975). Phys. Rev. B11, 197.
- Szwedler, A. R., Koenigsberg, S., Jorda, P. H., Vincenziani, R., and Johnston, D. C. (1977). Solid State Commun. 21, 1007.
- Toschell, L. P., Borelli, J. H., and Payer, W. A. (1973). Solid State Commun. 13, 1.
- Van Renth, L. C. and Koenigsberg, P. H. (1966). J. Appl. Phys. 37, 186.

- Wang, F. E. (1974). J. Phys. Chem. Solids 35, 273.
Wang, F. E. (1977). Solid State Commun. 23, 807.
Waterstat, R. M. and van Renth, E. C. (1966). Trans. Met.
A.I.M.E. 236, 1237.
Webb, G. W., Vieland, L. J., Miller, R. E., and Wicklund, A.
(1971). Solid State Commun. 9, 1769.
Willens, R. H. and Buehler, E. (1966). Trans. TMS A.I.M.E.
236, 171.

Figure Captions

Figure 1. A-15 structure showing orthogonal A and B axes.

Figure 2. Table of elements of groups 4A through 5B.

Figure 3. T_c versus c/a ratio for A-15 compounds.

Figure 4. Occurrence of binary s-d type A-15 compounds.

Figure 5. T_c versus composition range for s-p type A-15 compounds.

Figure 6. Variation of composition for a solid solution series of s-d type A-15 compounds.

Fig. 1.

Transition elements							Nontransition elements					
4A	5A	6A	7A	8A	9A	10A	1B	2B	3B	4B	5B	
A			B									
										Al	Si	P
Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	
Hf	Ta	W	Re	Cs	Ir	Pt	Au	Hg	Tl	Pb	Bi	

Fig. 2.

Fig. 3.

7A			8A			9A			10A		
Mn			Fe			Co			Ni		
							X			.57	
Tc			Ru			Rh			Pd		
					3.4	.38	.07	X	.03		
		13.4				2.5					
Re			Os			Ir			Pt		
	8.4			5.2	1.0	1.4	.7	.49	3.2	X	
		15.0		.94	11.7	1.3	5.1		10.0	4.5	
		11.4									

Ti	V	Cr
Zr	Nb	Mo
Hf	Ta	W

X - Elements

[5.2] A-15 phase
T_c = 5.2 K

[X] A-15 phase
normal T_c .015 K

Fig. 4.

Fig. 5.

Fig. 6.