

Superconductivity in Ti_3P -type compounds

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A study of 12 intermetallic A_3B compounds which crystallize in the tetragonal Ti_3P -type structure has revealed five new superconductors with transition temperatures below 1 K: Zr_3Si , Zr_3Ge , Zr_3P , V_3P , and Nb_3Ge (extrapolated from the alloy series Nb-Ge-As). In addition, two compounds, Zr_3Sb and Ta_3Ge , having the Ni_3P structure type were found to be superconducting below 1 K. Within the Ti_3P -type compounds, those with the lighter "B" elements in a given column of the Periodic Table have the higher transition temperatures. Critical-magnetic-field and electrical-resistivity data are reported for the superconducting Ti_3P -type compound Nb_3P which permit one to estimate the Ginzburg-Landau κ parameter and the electronic-specific-heat coefficient γ . The κ value of 8.4 indicates that this material is type II, and the γ value of 1.3 mJ/mole K^2 for Nb_3P is probably related to its low transition temperature relative to many $A15$ compounds.

I. INTRODUCTION

Intermetallic compounds having the A_3B stoichiometry and the $A15$ crystal structure are widely recognized for their exceptional superconducting properties. A elements in these compounds are invariably transition elements from columns IV, V, and VI in the Periodic Table. The best superconducting properties are obtained when the B element is a non-transition element from columns III, IV, and V.

There is another structure type, however, involving compounds of these same elements and possessing the same A_3B stoichiometry which has received much less attention. These are compounds which form in the tetragonal Ti_3P structure. Ti_3P -type compounds had not been known to be superconductors until recently when superconductivity was observed at about 0.3 K in the compounds Nb_3Si and Nb_3As .¹ Despite the relatively low superconducting transition temperatures (T_0) observed in these two compounds, it was felt that further studies should be made in view of the similarities in chemical composition between Ti_3P -type and $A15$ compounds. Thus, the present investigation was undertaken to ascertain if there are any systematics in the behavior of T_0 in the Ti_3P -type compounds, and to compare this behavior with the known behavior of $A15$ compounds having similar chemical compositions.

II. SAMPLE PREPARATION

The binary Ti_3P -type compounds used in this study were all prepared by arc melting in a high-purity

argon-helium atmosphere. Some ternary Ti_3P -type compounds were also prepared in this manner, but the ternary alloys contained extensive dendritic segregation which we were unable to eliminate by prolonged annealing at high temperature. An attempt was made to prepare Nb-Ta-Ge alloys by sintering the mixed elemental powders at 1600 °C for 24 h in a vacuum of 10^{-4} Pa (10^{-6} Torr). Single-phase samples could not be obtained since unreacted Nb or Ta was always present in substantial amounts as revealed by x-ray diffraction patterns. In the case of Nb-As-Ge alloys, these problems were solved by employing identical sintering conditions but using mixed powders of the binary alloys Nb_3As and Nb_3Ge which had been previously melted, annealed, and crushed to -325 mesh powder. X-ray diffraction patterns from each of the sintered Nb-As-Ge alloys revealed sharp lines of the Ti_3P -type structure and only a barely detectable trace of unreacted Nb. The x-ray patterns of the six Nb-As-Ge alloys revealed a continuous increase in the tetragonal c/a ratio of the Ti_3P -type structure with increasing Ge content from 0.505 for pure Nb_3As to about 0.508 for the most Ge-rich sample.

In the cases of the various binary Ti_3P -type compounds, great difficulties were encountered in preparing samples which were essentially single phase; this is apparently due to the extreme narrowness of the composition ranges for these compounds. Quantitative electron microprobe analyses were obtained on most of these samples and the Ti_3P -type compounds were invariably observed to have the stoichiometric (A_3B) composition within the analytical error ($\pm 1\%$). Thus any small deviation from this intended composition

produces substantial amounts of a second phase. In the A -rich alloys this second phase was usually in the form of a eutectic structure occurring at the grain boundaries of the Ti_3P -type phase and completely enveloping this phase. The eutectic structure is mainly composed of the primary A -rich solid solution, which has a relatively high zero magnetic field transition temperature T_0 . Such a dispersion of phases is unacceptable for the determination of T_0 by ac susceptibility techniques, as the network of higher T_0 material will effectively "shield" the superconducting transition of the lower T_0 material, i.e., the Ti_3P phase, enclosed by the network. A thin shell of high T_0 material will effectively shield the entire volume from any changes in magnetic flux ($\dot{B} = 0$). Thus the size of the signal will correspond to that which one would see if the "entire" volume went superconducting. This shell will shield the interior of the sample so that if the latter were to go superconducting, an ac technique would not detect it.

One common technique to avoid this shielding problem is to "powder" the samples. Rather than doing this however, we attempted to break up the shielding network by annealing at high temperatures. This breaks up the network phase into small isolated globules. This technique is effective only when the amount of second phase is relatively small ($< 5\%$ by volume). In most cases numerous adjustments in the alloy composition were required before the amount of second phase was reduced to an acceptable level. In B -rich alloys the second phase is usually not superconducting at the lowest temperatures obtainable (≈ 0.012 K), and consequently one can tolerate the presence of grain-boundary networks of these phases. Nevertheless, no samples were accepted for the T_0 measurements which showed evidence of a continuous grain-boundary network of a second phase.

It might be expected that serious problems would be encountered in melting alloys consisting of a high-melting-point A element and a volatile B element such as P or As. This is, in fact, true when one begins with the *pure elements*. For example, the pure elements were used in preparing the Ti_3As alloy and a large amount of As was volatilized during arc melting.² This loss had to be compensated for by repeated additions of As. Once the As had been combined with the Ti, however, the subsequent melting losses were sharply reduced. It appears that the vapor pressure of As in the compound Ti_3As is much less than that for pure As. This is apparently true for all of the Ti_3P -type compounds containing volatile elements since, once the compounds are formed, they can be remelted repeatedly with negligible weight loss.

In most cases, however, we did not begin with the pure elements but rather by melting the pure A element with a binary master alloy containing both the A and B elements in equiatomic proportions. These binary master alloys were obtained from a commercial

supplier who prepared them from the pure elements using a bomb reaction. These master alloys were analyzed by the manufacturer and had a certified purity of about 99.9%.

Each sample was submitted to examination by x-ray diffraction, metallographic, and quantitative electron microprobe analyses to ensure that the compound had been properly identified and was in suitable condition for the T_0 measurements. Interior fragments of the alloys were usually selected, and any exterior surfaces were removed by grinding prior to the T_0 measurements.

The x-ray diffraction powder patterns were obtained using $Cr K\alpha$ radiation in order to resolve the closely spaced lines of the Ti_3P -type structure. Considerable care is necessary in the interpretation of the powder x-ray diffraction patterns since line overlaps can occur not only from the presence of second phases or impurities but also from slight variations in the c/a ratios of the various Ti_3P -type compounds. Furthermore, the x-ray pattern of a Ti_3P -type structure closely resembles that of an Ni_3P -type structure when $c/a = 0.502$ and, in such cases, an unambiguous identification can be made only by obtaining data from a single crystal.

III. SUPERCONDUCTIVITY MEASUREMENTS

T_0 measurements were made at the Naval Research Laboratory (NRL). Temperatures below 1 K were produced by magnetic cooling techniques using chromium potassium alum (CPA) as the paramagnet. Using an NRL Bitter-type solenoid the CPA was isothermally magnetized to 3 T at 1.3 K, and then adiabatically demagnetized to zero magnetic field. The final temperature obtained by this technique was approximately 0.012 K. Temperatures were determined from the magnetic susceptibility of the CPA, which was in turn calibrated against 4He vapor pressure between 2.17 and 1.3 K. The T_0 measurements were made with a 97-Hz mutual inductance bridge using a measuring field of less than 10^{-6} T (10 mG). During the measurements the cryostat was enclosed by a mumetal shield which reduced the background field to the order of 10^{-6} T.

Thermal contact to the samples was made in the following manner. The samples were first lightly coated with Apiezon N grease, and then embedded in a bundle of several hundred 7.5×10^{-5} -m-diam bare copper wires. The other end of this copper wire bundle was in good thermal contact with the CPA pill, which had been previously grown on the wires.

A typical superconducting transition is shown in Fig. 1. The in-phase component of the magnetic susceptibility χ' is plotted as a function of the temperature for Zr_3Si . The transition temperature T_0 is defined as the midpoint of the susceptibility change and the width

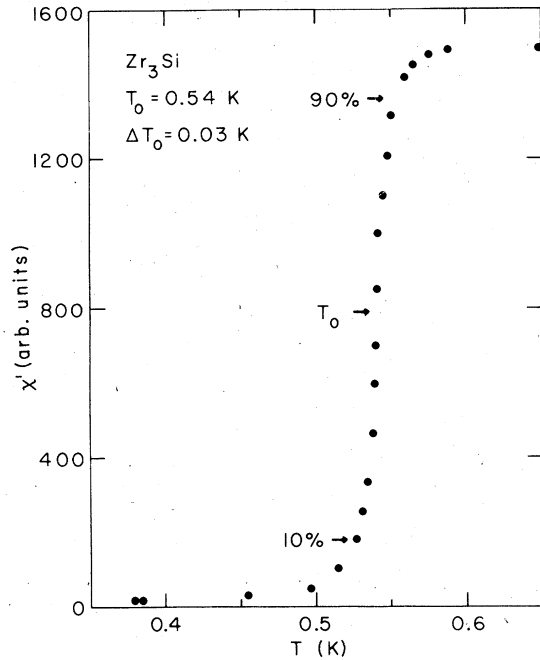


FIG. 1. Superconducting transition of Ti_3P -type Zr_3Si in zero magnetic field.

ΔT_0 is defined as the change in temperature between the 10% and 90% points of the curve.

Table I is a summary of the measurements on all the samples studied. The entry for Nb_3Ge is a value extrapolated from the ternary-alloy series measurements which will be discussed in Sec. V. Superconductivity has been observed previously in a tetragonal (probably the Ti_3P) structure type in Nb_3P and Ta_3P , the latter of which was not studied in this work.³ Those materials with very large transition widths ($\Delta T_0/T_0 > 0.2$) typically had transitions which were asymmetric in shape with a long high-temperature tail of superconductivity. Those materials listed as having a T_0 less than 0.01 K had susceptibility changes in the temperature range 30–0.01 K less than a few percent of that exhibited by a similar size and shape specimen which does become superconducting. Thirteen compounds were studied in this work, eight of which were found to be superconducting above 0.01 K.

IV. ADDITIONAL PARAMETERS FOR Nb_3P

We decided to characterize one of these compounds in greater detail, and chose Nb_3P because it had the highest T_0 as well as a relatively sharp transition. Additional measurements were thus made on Nb_3P to determine other superconducting and normal-state parameters. The resistance of a slab, cut from the cast sample by a diamond saw, was determined by a

TABLE I. List of crystal structures and superconducting parameters, for the compounds studied.

Compound	Structure	T_0 (K)	ΔT_0 (K)
Ti_3P	Ti_3P	<0.01	
Ti_3As	Ti_3P	<0.01	
Zr_3Si	Ti_3P	0.54	0.03
Zr_3Ge	Ti_3P	0.39	0.05
Zr_3P	Ti_3P	0.02	0.01
Zr_3As	Ti_3P	<0.01	
Zr_3Sb	Ni_3P	0.10	0.02
V_3P	Ti_3P	0.07	0.06
Nb_3Si	Ti_3P	0.29 ^a	0.02
Nb_3Ge	Ti_3P	<0.2 ^b	
Nb_3P	Ti_3P	1.83	0.11
		2.0 ^c	
Nb_3As	Ti_3P	0.31 ^a	0.06
Ta_3Si	Ti_3P	<0.01	
Ta_3P	Ti_3P	<0.01	
Ta_3Ge	Ni_3P	0.13	0.01
Ta_3P	Ti_3P	0.40 ^c	

^aReference 1.

^b T_0 extrapolated from the Nb-Ge-As alloy series.

^cReference 3.

standard four-probe technique. Resistivities at 300 and 4.2 K, $\rho(300)$ and $\rho(4.2)$, and the residual-resistance ratio are listed in Table II. Upper critical field (B_{c2}) values were determined by monitoring the ac bridge output (χ) as a function of dc magnetic field at constant temperature. Figure 2 is an x - y recording of the inductive component χ' and the loss component χ'' obtained by slowly increasing the magnetic field from zero. Figure 3 shows the temperature dependence of B_{c2} . Data points for temperatures higher than 1.75 K are significantly above the straight line, which is a hand-drawn fit to the data for temperatures less than 1.80 K. This high-temperature behavior may be due to variations in the critical-field curves of the various compositions inherent in this type of sample and reflected in the broad transition in zero field. In all the data χ' departed from its zero-field value in fields of about 1 mT. The slope of the line $(dB_{c2}/dT)_{T_0}$ is -0.181 T/K. This value together with $\rho(4.2)$ permits a calculation of the electronic coefficient of specific heat γ_v .

Combining the BCS expression⁴

$$(dB_{c2}/dT)_{T_0} = 1.34 \times 10^{-3} \gamma_v^{1/2}, \quad (1)$$

with the Abrikosov relation⁵

$$B_{c2} = \sqrt{2} \kappa B_c, \quad (2)$$

TABLE II. Material parameters for Nb₃P. The value for Θ is estimated from the Θ 's of similar T_0 A15 and Ti₃P-type compounds.

$\rho(300)$	2.86 $\mu\Omega$ m
$\rho(4.2)$	0.31 $\mu\Omega$ m
$\rho(300)/\rho(4.2)$	9.2
T_0	1.83 K
$\left(\frac{dB_{c2}}{dT}\right)_{T_0}$	-0.181 T/K
κ	≈ 8.4
γ_v	≈ 130 J/m ³ K ²
V_m	9.82×10^{-6} m ³
γ_m	≈ 1.3 mJ/mole K ²
Θ	400 K
λ	≈ 0.47
$N_{bs}(0)$	≈ 0.18 states/(eV atom)

where κ is the Ginzburg-Landau kappa parameter, one obtains

$$\left(\frac{dB_{c2}}{dT}\right)_{T_0} = 1.90 \times 10^{-3} \kappa \gamma_v^{1/2}, \quad (3)$$

with all quantities in Système International (S.I.) units. The value of κ can be obtained from the

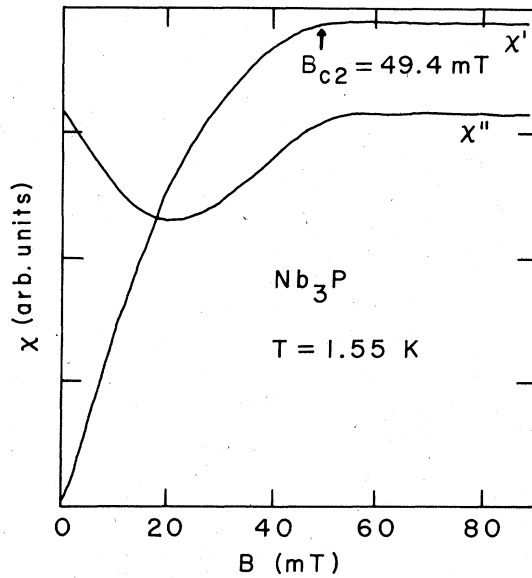


FIG. 2. Magnetic-field-induced superconducting-to-normal-state transition for Nb₃P. Both the inductive X' and the loss component X'' are shown. The critical magnetic field B_{c2} is defined as shown.

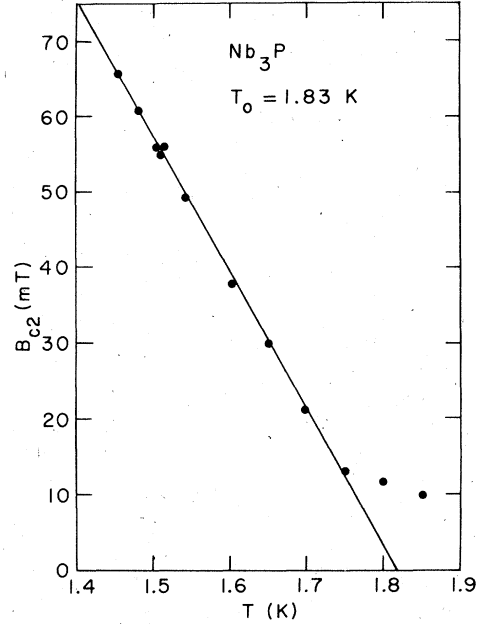


FIG. 3. Critical-magnetic-field curve for Nb₃P.

Goodman-Gorkov relation⁶

$$\kappa = 2.37 \times 10^6 \rho \gamma_v^{1/2}, \quad (4)$$

with ρ in Ω m and γ_v in J/m³K², valid in the dirty limit ($\kappa \gg 1$). Combining Eqs. (3) and (4) to eliminate κ between them, one arrives at the expression

$$\left(\frac{dB_{c2}}{dT}\right)_{T_0} = 4.5 \times 10^3 \gamma_v \rho. \quad (5)$$

The value of γ_v for Nb₃P obtained using this expression is 130 J/m³K². Substituting this value into Eq. (4) gives a κ value of 8.4. This may not quite be in the dirty limit; if it is not, the value of γ_v may be overestimated by perhaps (10–20)%.

The molar volume V_m of Nb₃P was calculated from the published values of the lattice parameters^{7–9} ($a = 1.0128$ nm and $c = 0.589$ nm) to be 9.83×10^{-6} m³/mole. The molar electronic specific-heat coefficient γ_m is 1.3 mJ/mole K².

Further estimates of material parameters can be made with the use of the McMillan equation¹⁰

$$T_0 = \frac{\Theta}{1.45} \exp\left[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right], \quad (6)$$

where Θ is the Debye temperature, μ^* is the Coulombic term (assumed here to be 0.13), and λ is the electron-phonon coupling constant. Although the value of Θ is not known for Nb₃P, a reasonable estimate of 400 K can be made based on low- T_0 A15 compounds and the Θ of 400 K for the Ti₃P-type compound Nb₃Si.¹ We obtain from Eq. (6) a value of 0.47

for λ . The band-structure density of states at the Fermi energy, renormalized for the effect of the electron-phonon interaction only, can be calculated from

$$N_{bs}(0) = 3\gamma_m(1 + \lambda)^{-1}/2\pi^2k_B^2, \quad (7)$$

where k_B is the Boltzmann constant, with the result of 0.18 states/(eV atom) for $N_{bs}(0)$. These calculated quantities are included in Table II.

V. DISCUSSION AND CONCLUSIONS

Probably the most remarkable result of this investigation is the low- T_0 values observed for Ti_3P -type compounds whose chemical composition would lead one to expect an exceptionally high T_0 if they possessed the *A15* crystal structure. For example, one observes a T_0 of ≈ 0.3 K for Nb_3Si despite the expectation of a T_0 exceeding 25 K in a hypothetical *A15*-type Nb_3Si .¹¹⁻¹³ It would be most interesting to determine the T_0 of a given A_3B compound which exists in both the Ti_3P -type and *A15* structures but, unfortunately, no such compound has yet been discovered. In keeping with this idea would be the determination of the T_0 of a hypothetical binary Nb_3Ge compound having the Ti_3P -type structure in order to compare it with the T_0 obtained for *A15*-type Nb_3Ge .

One could estimate T_0 for the missing Ti_3P -type or *A15* binary compounds by extrapolating data from appropriate ternary alloy systems. Extensive studies¹³ have revealed no ternary systems in which the *A15* phase region extends more than about 30% of the way toward the binary Nb_3Si , and therefore extrapolations would be extremely unreliable for this compound. It has been found in the present study, however, that the Ti_3P -type phase regions in the ternary systems $Nb-Ta-Ge$ and $Nb-As-Ge$ extend approximately 60% of the way toward the binary Nb_3Ge , and this seems sufficiently extensive to justify an extrapolation. The $Nb-Ta-Ge$ alloys, however, were inhomogeneous, and large superconducting to normal transitions were observed at about 4 K. These are apparently due to the (Nb,Ta) solid solution phase which is present in all of these samples. Additional smaller transitions were observed at about 0.35 and 0.17 K which could be due to the Ti_3P -type phase or to the coexisting ternary phase based on the A_5B_3 stoichiometry. In the $Nb-As-Ge$ alloys the high-temperature transition was either small or absent, and large transitions were observed which are believed to be due to the Ti_3P -type phase. These occur at about 0.9 K for the As-rich alloys and at 0.17 K for the most Ge-rich alloy, $Nb_3(As_{0.4}Ge_{0.6})$. The transition for the pure Nb_3As sintered powder sample, the end point of the $Nb-As-Ge$ series, begins around 2 K, has its midpoint at 1.0 K, and ends abruptly at 0.75 K. This contrasts with earlier work on cast and annealed Nb_3As which gave a T_0 of 0.31 K with a

width of 0.06 K. We believe that this difference in T_0 as well as the broad transition may be due to the existence of a relatively small composition range in Nb_3As which has a significant effect on T_0 . We preferred to use the value of $T_0 = 0.31$ K for Nb_3As since the "cast and annealed" sample has a sharp transition and is otherwise well characterized. The transitions of the ternary $Nb-As-Ge$ samples become extremely broad at intermediate compositions and in some cases, seem to disappear completely. This may be due to the mixing of As and Ge atoms on the *B* sites of this structure. The transition in $Nb_3(As_{0.4}Ge_{0.6})$, however, is relatively sharp, and we would therefore expect that this point is valid for an extrapolation. On this basis we estimate a T_0 of <0.2 K for hypothetical Ti_3P -type Nb_3Ge . This may be compared with a T_0 of 23.2 K observed in *A15*-type Nb_3Ge .^{14,15} Figure 4 shows the relationships within the Periodic Table of the known Ti_3P -type superconductors. The following systematic behavior is observed:

(i) Higher T_0 values are associated with the compounds containing the lighter *B* elements in each

Ti_3X		V_3X	
Si	P	Si	P
	<0.01 K	<i>A15</i>	0.07 K
Ge	As	Ge	As
	<0.01 K	<i>A15</i>	<i>A15</i>
Zr_3X		Nb_3X	
Si	P	Si	P
0.54 K	0.02 K	0.29 K	1.83 K
Ge	As	Ge	As
0.39 K	<0.01 K	<0.2 K	0.31 K
		Ta_3X	
		Si	P
		<0.01 K	0.4 K
		Ge	As
		<0.01 K	

FIG. 4. Superconducting transition temperatures of the Ti_3P -type compounds with the *A* elements and the *B*-element subgroups arranged as in the Periodic Table. Compounds labeled "A15" form in that crystal structure rather than the Ti_3P -type structure and are shown for completeness. We were unable to prepare Ti_3Si and Ti_3Ge , and we did not investigate Ta_3As .

column, and Nb_3P has the highest T_0 (1.83 K). A similar systematic behavior for light B elements is observed also in the $A15$ compounds, and this effect probably has a phononic origin.

(ii) Zr compounds with Si or Ge have higher T_0 values than those with P or As, whereas Nb compounds with P or As have higher T_0 values than those with Si or Ge. This behavior may be of electronic origin, but it does not seem to be an extension of the Matthias regularities, as there is poor correlation with the "electrons per atom" ratio in these compounds. Rather, it may reflect electronegativity relationships which produce electron-transfer between the A and B elements.¹⁶⁻¹⁸

(iii) Considering compounds with the same B element, one notes that compounds of V and Ta have lower T_0 values than those of Nb, and compounds of Ti have lower T_0 values than those of Zr. This is generally the case for $A15$ compounds also. This behavior may be due to differences in the electronic density of states for compounds of these elements.

(iv) No correlation with T_0 exists for either the atom-size ratios, the A - B electronegativity differences, or the axial ratios of the Ti_3P structure.

The Ti_3P structure type (Fig. 5) is closely related to the Ni_3P structure type, but useful comparisons of T_0 values cannot be made unless one considers only compounds of the same structure type. It appears in general that Ni_3P -type compounds tend to possess higher T_0 values than Ti_3P -type compounds, but much lower values than $A15$ compounds. This is supported by the data for the bimorphic compound Ta_3Ge , which has been tested in both the Ti_3P and Ni_3P structure modifications (see Table I). Ta_3Ge may also have been produced with the $A15$ structure in sputtered films which exhibit transitions beginning at 8 K and ending at about 1.5 K.¹⁹ However, the structure of these films is somewhat in doubt because no x-ray structure data were taken. It should also be noted that the T_0 for the Ni_3P -type compound Zr_3Sb is higher than would be expected for a Ti_3P -type compound in this B -element series. In general it appears that crystal structure is probably an important factor in determining the general level of the T_0 values. Thus the Ni_3P -type compounds generally seem to possess slightly higher T_0 values than the Ti_3P -type compounds. The closely related V_3S -type compounds could have higher T_0 values, and it may be noted that Mo_3P (a V_3S type)²⁰ has $T_0 = 5.43$ K.²¹ However, there are only a few compounds which possess the V_3S structure type, and for this reason comparison is difficult.

Lattice structure, however, may be only indirectly related to T_0 with the primary origin of high- T_0 values being the high electronic density of states which results from some prominent structural feature such as the mutually orthogonal atom chains in the cubic $A15$ structure. It is noteworthy that there are no atom

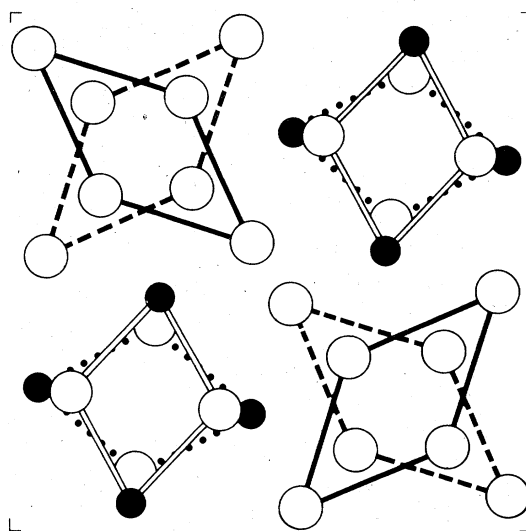


FIG. 5. Ti_3P -type crystal structure, as it appears in the compound Nb_3P viewed along the c axis. Small right angles mark the corners of the tetragonal unit cell. Large light circles represent Nb atoms, and smaller dark circles represent P atoms. The antisymmetrically superimposed diamonds in the upper-left and lower-right quadrants are made up of Nb(1) atoms (on the minor axis of each diamond) and Nb(3) atoms (on the major axis). These diamonds are located at $z = \frac{1}{4}$ (dashed lines) and $z = \frac{3}{4}$ (solid lines). Antisymmetrically superimposed diamonds exist also in the other two quadrants, but each diamond now contains both Nb(2) atoms (on the minor axis) and P atoms (on the major axis). These diamonds are located at approximately $z = \frac{1}{2}$ (parallel lines) and $z = 0$ or 1 (dotted lines). In the Ti_3P -type structure these two columns of superimposed diamonds are identical. In the Ni_3P -type structure the two columns are displaced relative to each other along the c axis by a distance of $\frac{1}{2}c$. This displacement would appear as an alternate 90° rotation of the columns when viewed along the c axis.

chains in the Ti_3P -type structure which are either linear or orthogonal.¹⁷

It has been suggested¹ that a strong electron-phonon interaction is mainly responsible for the existence of superconductivity in Ti_3P -type compounds since the ir electronic density of states is quite small compared to $A15$ compounds. In this connection it is noteworthy that Nb_3Si has a γ value of 2.15 mJ/mole K^2 ,¹ Nb_3P has a γ value of 1.13 mJ/mole K^2 , while the T_0 values are 0.29 and 1.83 K, respectively. Thus an increasing T_0 is associated with a decreasing electronic density of states which would imply that the electron-phonon interaction is extremely important for superconductivity in these compounds.

The strong electron-phonon contribution seems to be associated with light electronegative *B* elements. When this circumstance is combined with a high electronic state density, as in the *A15* compounds, the result is unusually high- T_0 values as in *A15*-type Nb_3Ge . When the structure does not give rise to a high electronic state density, as in the Ti_3P and Ni_3P compounds, one encounters low- T_0 values despite the strong electron-phonon interaction.

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²The compound Ti_3As has not been previously reported. We find that it has a Ti_3P -type structure with $a = 1.0187$ nm and $c = 0.5116$ nm.

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