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Effects of pressure on the structural and superconducting properties of Nb_3As, Nb_3Si, Nb_3Ge, and $Nb_{0.82}Ge_{0.18}$

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The effects of pressure on both the structure and superconducting transition temperatures (T_c) of several Nb-based compounds are examined. Comparisons are made between the Ti_3P-structure type, in which Nb_3As and Nb_3Si normally crystallize, and the *A*-15 structure in which Nb_3Ge and many other high-T_c materials form. A comparison is also made between stoichiometric and nonstoichiometric forms of the *A*-15 structure. The compressibilities are measured under hydrostatic pressures to about 6 GPa; the pressure dependencies of T_c are measured to about 10 GPa for the As and Si compounds and to about 1 GPa for the Ge compounds. The structural and electrical measurements are combined and the volume dependencies of T_c are reported and compared. Considerations are given to the possibility of a pressure-induced transition from the Ti_3P type to the *A*-15 structure for the As and Si compounds.

I. INTRODUCTION

Interest in the intermetallic A_3B compounds crystallizing in the *A*-15 structure has persisted for many years; several excellent review articles have appeared in the literature.[1-5] The extensive activity in this area was initiated largely by the discovery of high superconducting-transition temperatures in V_3Si ($T_c = 17$ K) by Hardy and Hulm[6] and in Nb_3Sn ($T_c = 18$ K) by Matthias, Geballe, Geller, and Corenzwit.[7] (The current accepted maximum value of T_c is 23.2 K for sputtered *A*-15 films of Nb_3Ge as reported by Testardi, Wernick, and Royer.[8]) Some of these compounds have relatively high-critical fields and currents, thereby further enhancing their potential utilitarian significance.

More recently, some attention has been focused on the stoichiometric compounds Nb_3As and Nb_3Si. Normally these compounds form in the tetragonal Ti_3P-type crystal structure as reported by Waterstrat *et al.*[9,10] and hereafter referred to simply as "Ti_3P structures." However, based on empirical arguments, it has been predicted that if these compounds were to form in the *A*-15, rather than the Ti_3P structure, they would then exhibit values of T_c in excess of 25 K.[5,11-13]

Details of the electronic and superconducting properties of these compounds have recently been discussed in some detail by Gubser, Hein, Waterstrat, and Junod.[14] It is the objective of this paper to consider possible interconnections between the electronic and structural properties which might be useful in predicting favorable conditions for formation of the *A*-15 structure. Specifically, the hydrostatic compressibilities of the Ti_3P structures, Nb_3As and Nb_3Si, are measured and compared with the *A*-15 compounds, $Nb_{0.82}Ge_{0.18}$ and the stoichiometric compound Nb_3Ge. This information is then correlated with the pressure dependence of T_c as measured from the same samples.

II. EXPERIMENTAL PROCEDURES AND RESULTS

A. Compressibility measurements

The Nb_3As and Nb_3Si samples used in this work were prepared at the Université de Genève from the constituent elementary components.[9] Details of the preparation of the Ti_3P-type structures are discussed elsewhere.[14] The stoichiometric and nonstoichiometric ($Nb_{0.82}Ge_{0.18}$) Ge samples were prepared by chemical-vapor-deposition (CVD) techniques described elsewhere[15] and by standard arc-melting methods, respectively.

The compressibility measurements were carried out by means of high-pressure x-ray diffraction techniques. The Nb_3As, Nb_3Si, and $Nb_{0.82}Ge_{0.18}$ samples were first mechanically ground and passed through a 400-mesh sieve and then thoroughly mixed with similarly prepared NaCl powder. Only limited quantities of the Nb_3Ge were available; these were used in the "as received" polycrystalline conditions. The polycrystalline mixtures were loaded in a diamond-anvil pressure cell and immersed in a hydraulic fluid (4 : 1 of methanol : ethanol by volume containing less than 10% glycerine) contained in a hardened metal gasket. A 4 : 1 methanol : ethanol mixture has a freezing pressure in excess of 10 GPa at room temperature,[16] thereby ensuring hydrostatic pressures for the compressibility data reported here. The pressure cavity was irradiated with Zr-filtered radiation from a Mo x-ray tube operated at 48 kV and 14 mA; the diffracted radiation was recorded photographically. Additional details of the high-pressure x-ray experimental techniques are discussed elsewhere.[17,18]

The linear compressibilities of the Ti_3P structures were determined from the pressure shift of the (201), (321), (112,330), (420), (411), and (222) diffraction lines. [The (112) and (330) lines could not be resolved on the high-pressure photographs.] A least-squares routine was used to find the axial lengths of the tetragonal unit cell at each pressure, $a(P)$ and $c(P)$. For the cubic Nb_3Ge and $Nb_{0.82}Ge_{0.18}$ samples, the (200), (210), (211), (220), and (310) lines were used to determine $a(P)$. The pressure was computed from the measured shift in the NaCl (111), (200), and (220) diffraction lines with the aid of the equation of state calculations of Decker.[19]

Compressibility data are presented graphically in Figs. 1 and 2. The uncertainties in the specific values of $a(P)$ and $c(P)$ reflect the quality of the aforementioned least-squares fits to the measured d spacings at each pressure; the overall experimental error can be estimated from the scatter in the data. In all cases, the measured fractional changes in the lattice parameters with pressure are represented by a linear function: the equations of these first-order curves were determined by a least-squares fit to the $\Delta a(P)/a_0$ and $\Delta c(P)/c_0$ values. Estimated values for the linear (k_a and k_c) and volume (K) compressibilities, based on these linear fits, are given in Table I.

It is noted that the compressibilities of all of the compounds are equivalent within their combined experimental uncertainties. Moreover, there is essentially no anisotropy in the linear compressibilities of the Ti_3P structures; thus one would expect the effect of hydrostatic pressure on these tetragonal structures to produce a uniform distortion of the lattice. Blaugher, Taylor, and Ashkin[20] have carried out compressibility studies on the A-15 structure of stoichiometric V_3Si. At 5 GPa they report a fractional change in the lattice parameter of about -10.5×10^{-3}. This is only slightly larger than the value of -7×10^{-3} observed here for both of the A-15 structures.

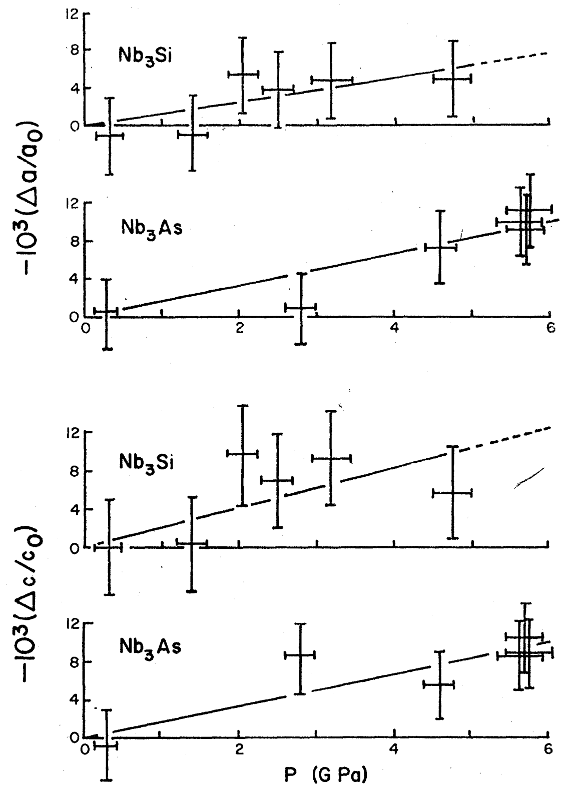

FIG. 1. Pressure dependence of the fractional change in the unit-cell parameters of Nb_3As and Nb_3Si.

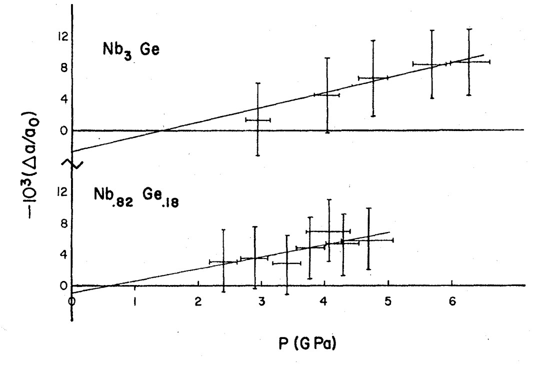

FIG. 2. Pressure dependence of the fractional change in the unit-cell parameter of Nb_3Ge (upper curve) and $Nb_{0.82}Ge_{0.18}$ (lower curve).

TABLE I. Compressibilities and pressure effects on T_c and λ for the compounds Nb_3As, Nb_3Si, Nb_3Ge, and $Nb_{0.82}Ge_{0.18}$.

	k_a (TPa^{-1})	k_c (TPa^{-1})	K (TPa^{-1})	T_c (K)	$\frac{dT_c}{dP}$ (K/TPa)	$\frac{d(\ln T_c)}{d(\ln V)}$	$\frac{d(\ln \lambda)}{d(\ln V)}$
Nb_3As	1.7 ± 0.3	1.7 ± 0.4	5.1 ± 1.0	~0.25	~10	~−8	~0.9
Nb_3Si	1.3 ± 0.05	2.1 ± 0.9	4.7 ± 1.9	~0.25			
Nb_3Ge	1.3 ± 0.2		3.9 ± 0.6	21.21 ± 0.03	−(116 ± 5)	1.4 ± 0.3	3.7 ± 0.4
$Nb_{0.82}Ge_{0.18}$	1.5 ± 0.3		4.5 ± 0.9	6.05 ± 0.03	−(353 ± 19)	13 ± 3	1.5 ± 0.2

B. Superconductivity studies

The effect of pressure on the superconducting-transition temperature, $T_c(P)$, of the Ti_3P structures was measured with a variable pressure, low-temperature diamond-anvil cell which was coupled to a dilution refrigerator.[21,22] In order to improve hydrostatic conditions on the brittle Ti_3P-structure superconductors, the samples were first powdered as discussed above, and then mixed with Cu powder of similar size to produce a more uniform distribution of pressure in the sample cavity. Nonhydrostatic strains of unknown magnitude were undoubtedly present. In *A*-15 compounds, strains tend to decrease T_c. Our measurements on the Ti_3P-compound, Nb_3As, show an increasing T_c; hence, we conclude that strain effects are not as important for these compounds as in the *A*-15 materials.

Pressure on the sample itself was estimated from the pressure acting on the bellows, which transmitted force to the diamonds, using a previously determined calibration.[21,22] An ac mutual-inductance technique was used to measure the superconducting transition and the temperature was determined from a calibrated carbon resistance thermometer.

Figure 3 shows the data, corrected to eliminate background signal, for the Nb_3Si and Nb_3As superconducting transitions. The in-phase or inductive output of the mutual inductance bridge is plotted (vertical axis) versus temperature for various pressure settings. These two compounds have previously been reported superconducting at temperatures near 0.3 K.[14] Data shown here indicate transition temperatures near 0.25 K. Two obvious differences between Nb_3Si and Nb_3As are apparent. First, the width of the Nb_3As transition is greater than that of Nb_3Si which may indicate a greater compositional variation within the Nb_3As sample or a higher concentration of defects introduced during formation of the compound. Secondly, whereas the transition temperature of Nb_3Si did not change within experimental error, Nb_3As showed a positive increase with pressure. (The diminuation of signal with pressure for the Nb_3Si sample can be explained by a rearrangement of the individual Nb_3Si particles as pressure was increased.)

Measurements of $T_c(P)$ for the Nb-Ge samples were made with ac mutual-inductance techniques with lock-in amplifiers to measure the in-phase and out-of-phase components of the magnetic susceptibility. The samples were clamped in a Be-Cu pressure bomb of the Chester type at room temperature. The samples were mixed with a pressure calibrant and immersed in a 1 : 1 mixture of pentane and isoamyl al-

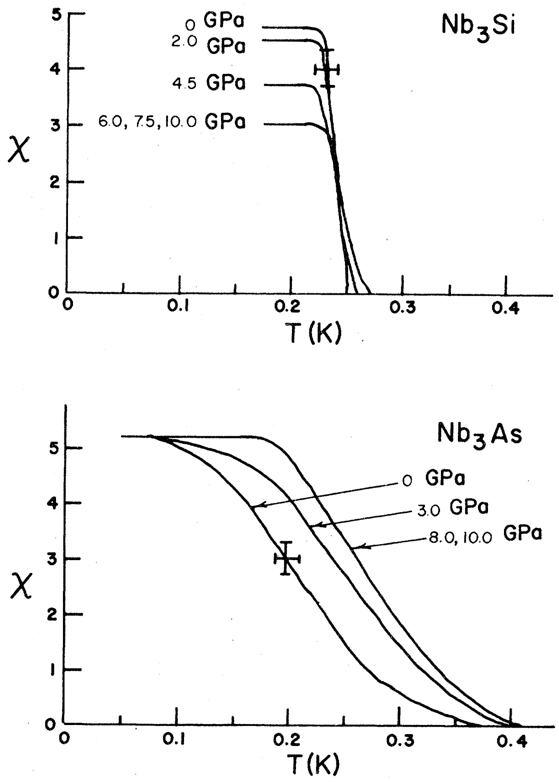

FIG. 3. Superconducting transitions for Nb_3As (lower curve) and Nb_3Si (upper curve) at various pressures.

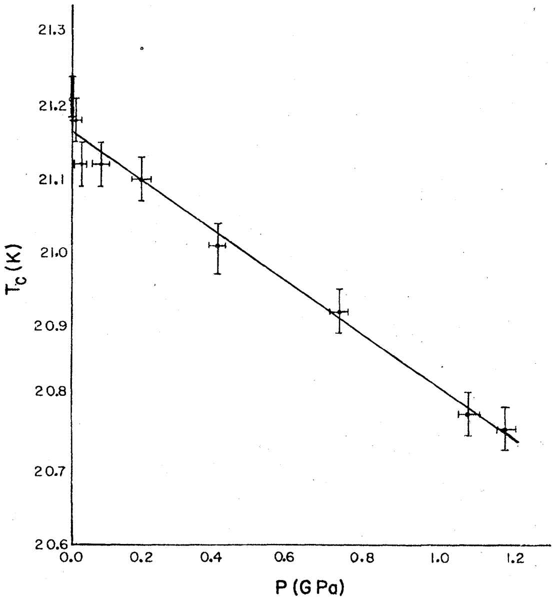

FIG. 4. Pressure dependence of the superconducting-transition temperature of Nb_3Ge.

cohol; thus a hydrostatic pressure was "frozen-in" as the bomb was cooled. The pressure calibrants were Pb and Sn for the Nb_3Ge and $Nb_{0.82}Ge_{0.18}$ runs, respectively. The width of the superconducting transitions were 0.3 to 0.4 K for Nb_3Ge, but only 0.1 K for the nonstoichiometric sample; the values of $T_c(P)$ were taken to be the midpoints of the transition curves. These data are plotted for the Nb-Ge samples in Figs. 4 and 5. For the Nb-Ge compounds, linear least-squares fits were made to the data shown in the figures. The results of these estimates and curve fits are tabulated in Table I. The dT_c/dP result shown for $Nb_{0.82}Ge_{0.18}$, viz., $-(116 \pm 5)$ K/TPa, compares very favorably with the value of -114 K/TPa reported by Smith[23] for essentially the same sample composition.

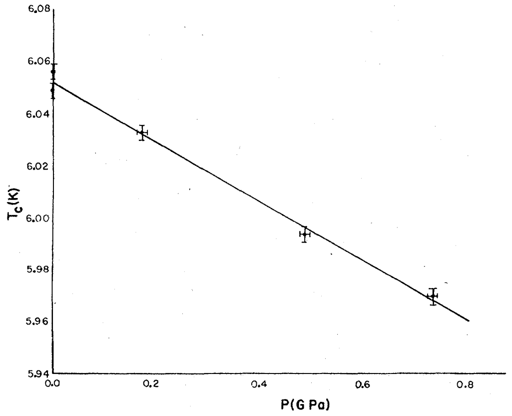

FIG. 5. Pressure dependence of the supercondicting-transition temperature of $Nb_{0.82}Ge_{0.18}$.

III. DISCUSSION

It has been known for some time that crystallization of an A_3B compound in the A-15 structure is apparently favored when the ratio of the atomic radii, $R(A)/R(B)$, is roughly within 10% of unity, here $R(A)$, $R(B)$ is the radius of the A, B atom.[24] (Although Johnson and Douglas[25] have noted that there are a significant number of exceptions to this empirical guideline.) The ratio of atomic radii of Nb to either Si or As may, however, approach or exceed 10% of unity[26] and the compounds Nb_3Si and Nb_3As do not normally exist in the cubic A-15 crystal structure but, as noted above, in the tetragonal Ti_3P structure. Considering for the moment only Nb_3Si, it was noted by Leger and Hall[27] that, since the initial- or low-pressure volume compressibility of Si was greater than Nb, then the R(Nb)/R(Si) ratio should increase with pressure making a pressure-induced phase change to the A-15 structure unlikely. However, in another article, Hall[26] noted that the atomic radius ratio at 10 GPa had actually decreased 3%, suggesting that pressures may in fact be beneficial in creating conditions favorable for a change to the A-15 structure. The entire concept of using atomic radii and elemental compressibilities to predict structural changes in complex compounds at high pressures is certainly questionable. The use of A-15 Geller radii[25,28] may be more justified for structure predictions in these compounds but no data on the pressure dependence of these radii exist.

Since, for Nb_3As and Nb_3Si at ambient pressure the Ti_3P structure is stable as compared to the A-15 structure, it may be supposed that the stable and metastable (denoted by an asterisk) forms have Gibbs free energies which differ by $G^0_{298}(Ti_3P) - G^0_{298}(A\text{-}15^*)$ at $P=0$, $T=298$K. The A-15 structure will be favored at high pressure if the density of the A-15 structure is higher than that of the Ti_3P structure $[(\partial G/\partial P)_T = V]$ and if the compressibility of the hypothetical A-15 structure is sufficiently low that the inequality of the volumes is retained $[K(Ti_3P) \sim K(A\text{-}15^*)]$ or even enhanced $[K(Ti_3P) < K(A\text{-}15^*)]$ at elevated pressures.

The compressibility data reported here support the idea that a pressure-induced structural instability may be produced in these Ti_3P compounds at elevated pressures. Based on the structural information of Waterstrat *et al.*,[4] the computed densities of Nb_3Si and Nb_3As (Ti_3P structure) are 7.517 $g\,cm^{-3}$ and 8.530 $g\,cm^{-3}$, respectively. However, based on the Geller relation[28] whereby the A-15 unit-cell dimensions can be determined from the A-B contact distance, the predicted unit-cell parameters of the corresponding A-15 structures are 5.08 and 5.12 Å, respectively, which yield A-15 densities of 7.78 and 8.75 $g\,cm^{-3}$, respectively. Thus in each case, the density of the Ti_3P structure is about 3% less than that predicted for the density of the A-15 structure. Since the compressibilities of the two structures appear comparable, it can be concluded that at elevated pressure, the A-15 structure will eventually become more stable than the Ti_3P and, further, that the decrease in the free energy arising from the volume reduction of the phase transformation will become increasingly greater with increasing pressure. However, it is also possible that other structures may be preferred at high pressures, so that the A-15 may not be stable at any pressure.

Pressure induced changes in the superconducting transition T_c of Nb_3Si, Nb_3As, Nb_3Ge, and $Nb_{0.82}Ge_{0.18}$ give further plausible evidence suggesting pressure stabilization of the A-15 phase. Pressure effects on the electron-phonon coupling parameter λ can be estimated from the approximate relation[29]

$$\frac{\partial \ln\lambda}{\partial \ln V} \approx \frac{\partial \ln T_c}{\partial \ln V} \Bigg/ \left[\ln\left(\frac{\Theta}{T_c}\right) f(\lambda,\mu^*) \right] ,$$

where

$$\frac{\partial \ln T_c}{\partial \ln V} = \frac{1}{K T_c} \frac{\partial T_c}{\partial P}$$

and, according to the McMillan strong coupling T_c formulation,

$$\Theta = \langle \omega \rangle / 1.2$$

and

$$f(\lambda,\mu^*) = \frac{\lambda(1+0.38)}{(1+\lambda)(\lambda-\mu^*-0.62\lambda\mu^*)} .$$

Here ω is a phonon frequency and μ^* is the Coulomb repulsion term.

The quantity $(\partial \ln\lambda/\partial \ln V)$ is related to changes in electronic and phonon properties through the relation

$$\frac{\partial \ln\lambda}{\partial \ln V} = \frac{\partial \ln\eta}{\partial \ln V} + \frac{\partial \ln(\langle \omega^{-2} \rangle)}{\partial \ln V} ,$$

where η is the product of the density of electronic states at the Fermi level $N(E_F)$ and the average electron phonon matrix element $\langle I^2 \rangle$

$$\eta = N(E_F) \langle I^2 \rangle .$$

According to recent band-structure calculations,[30] the quantity η is not expected to be particularly sensitive to volume changes for the A-15 Nb-Ge compounds since the Fermi levels fall in a broad minimum of the density-of-states curve. The volume dependence is thus expected to arise mainly from the $\langle 1/\omega^2 \rangle$ term. As the volume decreases, one generally expects $\langle 1/\omega^2 \rangle$ to decrease as the lattice begins to stiffen; hence, one anticipates the positive volume derivatives as observed. The large (factor of 2) difference in $\partial \ln\lambda/\partial \ln V$ between the high-T_c, stoichiometric compound and the low-T_c nonstoichiometric compound, suggests that the phonons are more sensitive to pressure in the high-T_c superconductor. This fact, in turn, suggests that the stoichiometric compound, which is a metastable phase, may be closer to a pressure-stabilized structural instability than the nonstoichiometric compound, i.e., it suggests that the stable high-pressure phase of stoichiometric Nb_3Ge is the A-15 structure. Evidence of a pressure-induced shift in the equilibrium A-15 phase boundary toward stoichiometric compositions has in fact been observed by Webb, Francavilla, Meussner, and Waterstrat.[31]

Preliminary experiments to produce the A-15 structure were carried out on Nb_3As and Nb_3Si at static pressures up to 20 GPa. However, x-ray diffraction patterns obtained at this pressure could still be indexed on the basis of the Ti_3P structure. It is possible, however, that kinetic factors prevented the transition from taking place.

At higher temperatures, e.g., close to the melting temperature, where kinetic factors are favorable, it is possible that the pressure needed to form the A-15 phase will be reduced. For this to occur the entropy of the A-15 phase must be lower than the Ti_3P phase. Using a Debye model for the specific heat, it is required that the Debye temperature be higher for the A-15 phase than for the Ti_3P phase. Since the compressibilities are similar, the inequality will possibly hold because of the above relationship between the densities.

Although the foregoing remarks are in the nature of tentative speculations, they give some impetus to an experimental program of synthesis at high temperatures and pressures. It is noted that two successful efforts of transforming Nb_3Si at elevated pressures have been reported: Pan, Alekseevskii, Popov, Beletskii, Yupko, and Yarosh[32] reported forming Nb_3Si in the A-15 structure through application of shock explosion techniques where estimated pressures in excess of 50 GPa were produced. Very recently, Dew-Hughes and Linse[33] have confirmed the results of Pan *et al.* by transforming Nb_3Si from the tetragonal structure to a high-T_c superconductor (onset of 18 K) by explosive pressures approaching 100 GPa.

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