

# Superconductivity at High Pressure in the A15 Compounds\*

T. F. Smith

*Institute for Pure and Applied Physical Sciences,  
University of California, San Diego, La Jolla, California*

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*The superconducting transition temperature for a number of A15 compounds has been determined as a function of hydrostatic pressure up to 25 kbar. The observed pressure dependences are compared with the predictions of a number of correlations between  $T_c$  and volume derived from zero-pressure data. The limitations of the theoretical models used to calculate  $T_c$  for the transition metals and their alloys when applied to a description of the pressure dependence are discussed.*

## 1. INTRODUCTION

The compounds with the A15 ( $\text{Cr}_3\text{Si}$  type) structure have been found to be particularly favorable for the occurrence of superconductivity.<sup>1,2</sup> The discovery of most of the materials with the highest known transition temperatures in this group of compounds has led to a considerable interest in their physical properties, both in the normal and superconducting states, with the hope that a sufficient understanding of their properties would ultimately lead to higher transition temperatures. Although considerable insight has been achieved, particularly with respect to the strong temperature dependence of the physical properties, which is observed for most of the high  $T_c$  compounds, the controlled increase of the superconducting transition temperature, from a theoretical basis, has yet to be realized. Consequently, a number of empirical approaches have been tried in which  $T_c$  is correlated to some other physical parameter. The most successful of these approaches is that of Matthias<sup>3</sup> in which  $T_c$  is plotted against the mean-valence-electron-per-atom ratio ( $e/a$ ) and which finally lead to the discovery<sup>4</sup> of the highest yet known  $T_c$  ( $\sim 21$  K) for the ternary A15 compound

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$\text{Nb}_3\text{Al}_{0.75}\text{Ge}_{0.25}$ . Variations on the Matthias scheme have been proposed in which the atomic volume<sup>2</sup> is included, and attempts have also been directed towards a direct correlation of  $T_c$  with lattice parameter.<sup>5,6</sup>

Surprisingly, in spite of the attempts to correlate  $T_c$  with lattice volume, very little effort has been directed towards the examination of the influence of pressure on the superconductivity or the normal state properties of the A15 compounds. This paper presents the results of an investigation of the pressure dependence of  $T_c$  for a number of A15 compounds. These measurements are compared with predictions derived from correlations of  $T_c$  with volume, as based on alloying studies, and are discussed in relation to theoretical models which have been used to account for the superconducting and normal state properties.

## 2. EXPERIMENTAL DETAILS

### 2.1. High-Pressure Stage

A clamp device, in which the pressure applied at room temperature by a standard press may be locked, permitting the removal of the high-pressure stage from the press and its transfer to a cryostat, was used for the pressure measurements. The pressure was contained in a 1 in. o.d.,  $\frac{1}{4}$  in. i.d. cylinder fabricated from Berylco 25, Cu-Be alloy hardened to 40-43 Rockwell C. The cylinder bore was initially made 0.02 in. undersize and the working volume prestressed to  $\sim 30$  kbar using tin as a pressure medium. This stretched the bore by 0.010-0.015 in., which was then turned out to 0.250 in. Following this treatment it is found that such a cylinder may be used repeatedly to 20 kbar with only a slight expansion of the bore. Pistons were cut from stock Carboloy 883 $\frac{1}{4}$  in. diameter rod.

The samples were contained in a Teflon capsule which was filled with with a 1:1 mixture of *n*-pentane and isoamyl alcohol.<sup>7</sup> The capsule is self-sealing under pressure and only standard high-pressure sealing rings are required to stop the extrusion of the capsule past the pistons. Since the pressure medium remains fluid at room temperature to 35 kbar the pressure is applied hydrostatically. Thus, the only deviation from hydrostatic conditions at the low temperature results from the freezing of the fluid and its subsequent thermal contraction relative to the sample, on cooling.

A close examination of a sharp-edged cube of In, cut to the approximate dimensions of the average sample (1-2 mm side) revealed no evidence of any deformation after being cooled to its transition temperature ( $\sim 2.6$  K) at 25 kbar. Furthermore, the zero pressure  $T_c$  was observed to be reproducible on release of the pressure, in this and previous investigations, even for materials for which large irreversibilities have been observed when using solid pressure transmitting media. It is concluded, therefore, that even at

low temperature the deviation from hydrostatic conditions around the sample must be slight and certainly does not appear to be sufficient to influence the determination of  $T_c$ .

No special effort was made to slow cool the pressure cell since no difference could be distinguished between transitions measured after cooling to liquid-nitrogen temperature over several hours or several minutes. Thus, the normal procedure adopted was to precool the clamp by direct immersion in liquid nitrogen and then transfer it to a Dewar containing liquid helium. The total cooling time from room temperature to 4 K was usually on the order of 30 min.

The samples were either in the form of small arc-melted buttons or irregular-shaped pieces and had volumes of  $\sim 10^{-2} \text{ cm}^3$ . By making a suitable choice of samples so as to avoid the overlapping of transitions it was possible to work with up to four samples and a manometer in a single pressure run. The total sample volume never exceeded 20% of the capsule volume.

The pressure at the low temperature was determined relative to the superconducting transition temperature of tin or lead,<sup>8</sup> depending on whether measurements were being made above or below 4.2 K.

## 2.2. Cryostat and Temperature Measurement

The cryostat consisted of a pair of simple, open-ended glass Dewars, thus permitting easy access to the helium space at room temperature. Measurements below 4.2 K were made with the clamp immersed in the helium bath, the temperature of which could be lowered to  $\sim 0.97 \text{ K}$  by means of a pumping system incorporating an Edwards Speedivac booster pump (model 9B3). For measurements above 4.2 K the clamp was suspended above the helium bath, the distance from the liquid surface serving as a rough temperature control. Finer adjustment of the temperature was achieved by a combination of pumping on the bath through a needle valve and varying the radiation from an infrared heat lamp which was shone in through the observation slits in the Dewar walls. Temperature uniformity of the clamp was aided by a surrounding copper shield. The temperature drift could be readily controlled to permit a slow passage back and forth through the superconduction transition curve, and traces were taken until the hysteresis was reduced to  $< 10\%$  of the transition width.

Temperatures below 4.2 K were determined directly from the pressure over the helium bath using the 1958 helium vapor-pressure scale. Above 4.2 K the temperature was determined from a germanium resistance thermometer calibrated from 2–4.2 K against the helium vapor-pressure scale and from 14–20 K against the equilibrium hydrogen vapor-pressure scale of Durieux.<sup>9</sup> Point calibrations were also made at the superconducting

transitions of lead and niobium, where  $T_c$  values of 7.193 K<sup>10</sup> and 9.207 K,<sup>11\*</sup> respectively, were assumed from determinations made relative to the helium gas thermometer. The transition temperature of Pb was measured a number of times during the course of the investigation and served as a check on the stability of the calibration. The maximum variation recorded was  $\pm 1 \Omega$ , which is equivalent to  $\pm 5$  mdeg.

The resistance-temperature calibration data were least-squares fitted to the relationship

$$\log R/T = \sum_{n=0}^m a_n (\log R)^n$$

over the temperature ranges 3–9 K ( $m = 10$ , standard deviation 4.5 mdeg) and 7–20 K ( $m = 6$ , standard deviation 5.5 mdeg), with suitable adjustment to give good agreement between the two fits in the overlap region.

### 2.3. Transition Measurement

The transition to the superconducting state was monitored from the output of a mutual inductance coil surrounding the high-pressure cylinder, the sample being located in one of a pair of opposed secondaries. After phase-sensitive detection and suitable amplification the signal was fed onto the Y axis of a X–Y recorder, the X axis of which was driven by the amplified voltage drop across the germanium thermometer. Thus, a continuous trace through the transition curve was obtained.

### 2.4. Sample Preparation

A number of the samples were obtained from several sources and are often part of material used in earlier investigations. The majority of these samples had been prepared by melting the constituents in an argon arc furnace, as were the samples which were specifically prepared in the course of the present investigation. The weight losses occurring during melting were usually negligible, and the nominal compositions are assumed to be correct. Those samples which were annealed after casting were wrapped in Ta or Zr foil and sealed in evacuated quartz tubes. The annealing temperatures and times required to influence the degree of atomic order and the value of  $T_c$  were taken from published data. The generally close agreement between the  $T_c$  values found in this investigation and those of previous investigations on well characterized samples for which structure determinations had been made was taken as sufficient indication that the samples were in the A15

\*The niobium used for the calibration was part of the material for which the absolute determination of  $T_c$  was made and was kindly supplied by Dr. Finnemore.

phase. Thus, x-ray measurements were not normally made, though the lattice parameter for some samples was known from previous investigations.

### 3. RESULTS

A complete listing of all of the compounds investigated with the initial zero pressure  $T_c$ , the width of the transition  $\Delta T_c$ , the pressure dependence  $\partial T_c / \partial P$ , and a summary of the heat treatment are presented in Table I. Except where indicated  $T_c$  is taken to be the midpoint of the linear portion of the transition curve, extrapolated to intersect the extrapolation of the normal and superconducting state traces. Measurements of  $T_c$  were generally made in approximately 5-kbar intervals up to 20 or 25 kbar. In many cases the zero-pressure transition was then redetermined after release of the pressure. On no occasion was any significant irreversibility observed. With one exception  $T_c$  was found to vary linearly with pressure, and the quoted values of  $\partial T_c / \partial P$  represent the "by eye" best-fit lines drawn through the data.

As the majority of the compounds studied form the A15 structure directly on cooling from the melt, measurements were usually made initially in the as-cast condition. In view of the influence of atomic ordering on  $T_c$  a number of the samples were also examined after annealing, brief details of which are given in Table I. To avoid the possibility of any problems associated with compositional variations successive heat treatments and measurements were made on the same sample. It is indicated in the table where more than one sample of a particular compound was investigated.

The specific details for each group of compounds are given below.

#### 3.1. Vanadium

##### 3.1.1. V-Si

The single crystal  $V_3Si$  sample which was examined was in the form of a 3-mm-diam, 3-mm-long cylinder which had been spark cut from the center of a slice taken off the end of a large single crystal rod grown by E. S. Greiner. Heat capacity measurements<sup>12</sup> made on a small piece of material cut from the remainder of the disk show no evidence of the cubic to tetragonal transformation that occurs just above  $T_c$  for polycrystalline material and many, but not all, single crystals.<sup>13</sup> It is assumed, therefore, that the sample used for the pressure measurements is also nontransforming. The  $T_c$  value of 16.85 K is somewhat lower than values quoted by Testardi *et al.*<sup>6</sup> for other nontransforming crystals.

The as cast A15 phase polycrystal sample of  $V_3Si$  has a lattice parameter of 4.725 Å and  $T_c = 16.83$  K, both in excellent agreement with other

TABLE I

Superconducting Transition Temperature  $T_c$ , Transition Width  $\Delta T_c$ ,  $\partial T_c / \partial P$ , and Heat Treatment for the A15 Compounds Investigated

| Compound                                                      | $T_c$ ,<br>K       | $\Delta T_c$ ,<br>K | $\partial T_c / \partial P$ ,<br>$10^{-5} \text{ K} \cdot \text{bar}^{-1}$ | Heat treatment                      |
|---------------------------------------------------------------|--------------------|---------------------|----------------------------------------------------------------------------|-------------------------------------|
| $\text{V}_3\text{Si}$ (single crystal) <sup>a</sup>           | 16.85              | 0.01                | $3.7 \pm 0.1$                                                              |                                     |
| $\text{V}_3\text{Si}^b$                                       | 16.83              | 0.15                | $3.1 \pm 0.2$                                                              |                                     |
| $\text{V}_{0.78}\text{Si}_{0.22}^b$                           | 14.38 <sup>c</sup> | $\sim 2$            | $2.6 \pm 0.2$                                                              |                                     |
| $\text{V}_3\text{Ga}^b$                                       | 13.87              | 0.34                | $1.05 \pm 0.05$                                                            |                                     |
| $\text{V}_3\text{Sn}^b$                                       | 3.650              | 0.010               | $0.49 \pm 0.02$                                                            |                                     |
| $\text{V}_3\text{Ge}^b$                                       | 6.10               | 0.03                | $8.10 \pm 0.15$                                                            |                                     |
| $\text{V}_3\text{Ge}_{0.9}\text{Al}_{0.1}^d$                  | 8.80               | 0.7                 | $3.47 \pm 0.05$                                                            |                                     |
| $\text{V}_3\text{Ge}_{0.8}\text{Al}_{0.2}^d$                  | 11.02              | 0.1                 | $2.53 \pm 0.05$                                                            |                                     |
| $\text{V}_3\text{Ge}_{0.7}\text{Al}_{0.3}^d$                  | 11.17              | 0.3                 | $2.63 \pm 0.10$                                                            |                                     |
| $\text{V}_3\text{Au}^b$                                       | $< 0.97$           |                     |                                                                            |                                     |
|                                                               | 1.755              | 0.014               | $0.875 \pm 0.015$                                                          | 800°C, 1 day                        |
|                                                               | 2.731              | 0.039               | $1.3 \pm 0.01$                                                             | 600°C, 4 weeks                      |
| $\text{V}_3\text{Pt}^b$                                       | 2.630              | 0.13                | $-0.41 \pm 0.03$                                                           |                                     |
|                                                               | 3.180              | 0.13                | $-0.86 \pm 0.06$                                                           | 800°C, 2 days                       |
| $\text{V}_{0.67}\text{Ir}_{0.33}$                             | 1.60               | 0.25                | $-0.21 \pm 0.04$                                                           |                                     |
| $\text{Nb}_3\text{Sn}^e$                                      | 17.832             | 0.017               | $-1.4 \pm 0.15$                                                            | sintered                            |
| $\text{Nb}_3\text{Al}^f$                                      | 17.11              |                     | $-0.7$                                                                     |                                     |
| $\text{Nb}_3\text{Ge}$                                        | 6.281              | 0.036               | $-1.14 \pm 0.06$                                                           |                                     |
| $\text{Nb}_{0.78}(\text{Al}_{0.75}\text{Ge}_{0.25})_{0.22}^b$ | 20.29 <sup>c</sup> | $\sim 1.5$          | $-0.2 \pm 0.1$                                                             |                                     |
| $\text{Nb}_3\text{Ga}^b$                                      | 14.54              | 0.35                | $-0.70 \pm 0.05$                                                           |                                     |
| $\text{Nb}_3\text{Au}^b$                                      | 11.076             | 0.020               | $0.39 \pm 0.01$                                                            |                                     |
|                                                               | 11.226             | 0.030               | $0.42 \pm 0.01$                                                            | 780°C, 12 days                      |
| $\text{Nb}_3\text{Ir}$                                        | 2.07               | 0.15                | $0.55 \pm 0.05$                                                            |                                     |
| $\text{Nb}_3\text{Rh}$                                        | 2.797              | 0.012               | $-0.32 \pm 0.02$                                                           |                                     |
| $\text{Nb}_3\text{Pt}$                                        | 8.111              | 0.040               | $-0.63 \pm 0.01$                                                           |                                     |
|                                                               | 8.174              | 0.025               |                                                                            | 800°C, 1 day                        |
|                                                               | 10.53 <sup>c</sup> | 0.35                | $1.88 \pm 0.1^h$                                                           | 900°C, 10 days                      |
| $\text{Ta}_3\text{Sn}$                                        | 5.82               | 0.07                | $-1.16 \pm 0.05$                                                           | sintered, 650°C, 1 day, 1200°C, 5 h |
| $\text{Ti}_3\text{Sb}^b$                                      | 5.10               | 0.10                | $-0.05 \pm 0.05$                                                           |                                     |
|                                                               | 5.47               | 0.20                | $0.16 \pm 0.03$                                                            | 800°C, 36 h                         |
| $\text{Ti}_3\text{Ir}^g$                                      | 4.970              | 0.030               | $1.47 \pm 0.02$                                                            | 1000°C, 1 day                       |
|                                                               |                    |                     |                                                                            | 600°C, 2 weeks                      |
| $\text{Cr}_{0.72}\text{Ru}_{0.28}^d$                          | 3.468              | 0.003               | $0.130 \pm 0.005$                                                          | 900°C, 1 month                      |
| $\text{Cr}_{0.72}\text{Os}_{0.28}$                            | 3.862              | 0.020               | $0.06 \pm 0.01$                                                            | 1200°C, 1 day, quenched             |
| $\text{Mo}_3\text{Si}$                                        | 1.402              | 0.060               | $-0.35 \pm 0.04$                                                           |                                     |
| $\text{Mo}_3\text{GeI}$                                       | 2.166              | 0.050               | $-0.45 \pm 0.01$                                                           |                                     |
| $\text{Mo}_3\text{Ge2}$                                       | 1.600              | 0.10                | $-0.47 \pm 0.02$                                                           |                                     |
| $\text{Mo}_3\text{Os1}^g$                                     | 11.69              | 0.07                | $-0.95 \pm 0.04$                                                           | 1800°C, 2 h, 600°C, 2 weeks         |
| $\text{Mo}_3\text{Os2}^i$                                     | 12.50              | 0.03                | $-0.96 \pm 0.04$                                                           | 2000°C, 4 h, 1100°C, 2 weeks        |
| $\text{Mo}_3\text{Ir}^g$                                      | 8.174              | 0.030               | $-0.81 \pm 0.05$                                                           | 1800°C, 2 h, 600°C, 2 weeks         |

(See footnotes opposite)

determinations.<sup>14-17</sup> The  $V_{0.78}Si_{0.22}$  sample has a broad transition, but the onset is well defined, so this has been taken as a measure of  $T_c$  for the determination of the pressure dependence.

The transition curves for both the polycrystal and single crystal  $V_3Si$  exhibit broadening under pressure, amounting to approximately a doubling of the transition width at 20 kbar. In the case of the single crystal this is accompanied by a change in the overall shape of the transition, as may be seen in Fig. 1, where transition curves recorded at various pressures are presented. However, in spite of this broadening, there can be no doubt that there is a general shift of the transition, as a whole, to higher temperatures. It may also be noted that on release of the pressure the transition almost returns to its initial width.

From measurements to 2 kbar using the ice-bomb technique, Müller and Sauer<sup>18</sup> obtained a value of  $\partial T_c / \partial P = -2.1 \times 10^{-5} \text{ K} \cdot \text{bar}^{-1}$  for a polycrystal sample of  $V_3Si$ , formed as a surface layer on vanadium wire. Weger, Silbernagel, and Greiner<sup>19</sup> studied the effect of both hydrostatic and uniaxial stress on the  $T_c$  of single crystal  $V_3Si$ . They found that a stress of  $\sim 0.5$  kbar, applied along the [100] direction, lowered  $T_c$  at a rate of  $-5 \times 10^{-4} \text{ K} \cdot \text{bar}^{-1}$ , whereas a similar stress applied along the [111] direction had very little effect on the transition. The application of a hydrostatic pressure of  $\sim 0.4$  kbar using helium gas as the pressure medium produced no detectable shift of the transition to within their temperature resolution of  $\pm 0.05$  K. In the most recent determination Neubauer<sup>20</sup> has reported  $\partial T_c / \partial P = 2.3 \times 10^{-5} \text{ K} \cdot \text{bar}^{-1}$  from measurements on polycrystal  $V_3Si$ , employing a pressure transmitting medium similar to that used in the present study.

In view of the observations of Weger *et al.* we would explain the discrepancy between the result of Müller and Sauer and those of Neubauer and the present determination as due to the poorer hydrostatic pressure conditions in the former workers' experimental arrangement. The nature of their samples could lead to quite a considerable stress inhomogeneity at the boundary between the wire and the surface layer. Furthermore, it is questionable as to how hydrostatic is the pressure distribution which is

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<sup>a</sup>Sample supplied by E. S. Greiner, Bell Telephone Laboratories, Murray Hill, N.J.

<sup>b</sup>Sample supplied by E. Corenzwit, Bell Telephone Laboratories, Murray Hill, N.J.

<sup>c</sup>Transition onset.

<sup>d</sup>Sample supplied by H. L. Luo, AP&IS Department, UCSD, La Jolla, California.

<sup>e</sup>Sample supplied by L. Vieland, RCA Laboratories, Princeton, N.J.

<sup>f</sup>Data from Ref. 20.

<sup>g</sup>Sample supplied by S. L. McCarthy, State University of New York, Stony Brook, N.Y.

<sup>h</sup>Initial slope, see text for details.

<sup>i</sup>Sample supplied by D. Johnston, Physics Department, UCSD, La Jolla, California.

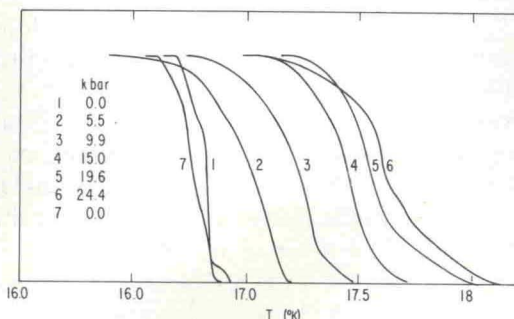


Fig. 1. Transition curves at various pressures for single crystal  $V_3Si$ .

produced in the ice-bomb arrangement. From the uniaxial stress measurements it is estimated that a 10% inhomogeneity in the stress distribution *within* the sample would be sufficient to account for the decrease of  $T_c$  observed by Müller and Sauer, if the present value is taken to be the true hydrostatic dependence. This sensitivity of  $T_c$  to the internal stress distribution is the most probable explanation of the 37% numerical difference between the present value for  $\partial T_c / \partial P$  and that of Neubauer and the broadening of the transition curves as the pressure is increased. It may also be noted that the change of  $T_c$  ( $\sim 0.02$  K) which is expected for the hydrostatic pressure which was applied by Weger *et al.* lies well within their quoted resolution.

An indirect determination of the pressure dependence of  $T_c$  for non-transforming single crystal  $V_3Si$  has been derived by Testardi and co-workers<sup>6</sup> from the change in the velocity of sound and by Fawcett<sup>21</sup> from the change in the thermal expansion at the superconducting transition by means of the appropriate thermodynamic relationships. The elastic data suggest a form for the pressure dependence of  $T_c$  which is quite contrary than that observed, but as an extensive analysis of the discrepancies associated with the thermodynamic treatment has already been given<sup>22</sup> no further discussion will be undertaken here.

### 3.1.2. $V-Ga$

The  $T_c$  value for our as cast A15 phase  $V_3Ga$  sample is in good agreement with that reported by Müller,<sup>16</sup> but somewhat lower than that found by Junod *et al.*<sup>17</sup> for annealed samples. The lattice parameter for our sample was determined to be  $4.816 \text{ \AA}$ , again in good agreement with the value given by Müller but smaller than that reported by Junod *et al.*

The present observation of a positive pressure dependence for  $T_c$  is again in conflict with the negative pressure dependence reported by Müller

and Sauer<sup>18</sup> for  $V_3Ga$  formed as a surface layer on vanadium wire. Uniaxial stress measurements have not been made for this compound, but it is expected that the discrepancy has a similar origin to that in the case of the  $V_3Si$ .

### 3.1.3. $V-Sn$

Our as cast sample of  $V_3Sn$  has a  $T_c$  value of 3.65 K, which is close to the value of 3.80 K reported by Cody *et al.*<sup>24</sup> and by Spitzli<sup>23</sup> from heat capacity measurements on an annealed A15 phase sample. These values are considerably lower than the initial value of 7.0 K given by Geller *et al.*<sup>25</sup>

### 3.1.4. $V-Ge$

Our as-cast A15 phase  $V_3Ge$  sample has a lattice parameter of 4.783 Å and a  $T_c = 6.10$  K, both quantities being in a good agreement with a number of previous determinations.<sup>16,23,26</sup>

Elastic data have also been used to derive<sup>6</sup> the form of the pressure dependence of  $T_c$  for  $V_3Ge$ , but as these measurements have also been discussed<sup>22</sup> along with those for the  $V_3Si$  no further comment will be made here.

### 3.1.5. $V-Ge-Al$

Substitution of Al for Ge expands the lattice and causes a marked increase of  $T_c$ .<sup>16,26,27</sup> The pressure measurements were made<sup>28</sup> on a series of  $V_3Ge_{1-x}Al_x$  alloys, which were prepared during an earlier investigation<sup>26</sup> of this system, in order to test the suggestion<sup>6</sup> that  $T_c$  was directly related to the lattice dimension. It is seen that compression of the lattice for the ternary compounds does not reverse the increase of  $T_c$  which occurs when the lattice expands with the substitution of Al for Ge. It is concluded, therefore, that the transition temperature is dependent on more than simply the lattice dimension.

### 3.1.6. $V-Au$

Superconductivity was not detected down to 0.97 K at zero or 25 kbar pressure for the as-cast  $V_3Au$ . The zero-pressure observation is consistent with the reported  $T_c$  values around 0.85 K for the as-cast state.<sup>1,23,29</sup> Following the annealing procedure outlined by Blaugher *et al.*<sup>29</sup> a 1-day anneal at 800°C resulted in a  $T_c$  value of 1.755 K. After pressure measurements to 20 kbar the zero-pressure transition was checked and found to be reproducible to within a few millidegrees. The sample was then given a further anneal at 600°C for 4 weeks, after which  $T_c$  had increased to 2.731 K.  $\partial T_c / \partial P$  was remeasured and found to have increased by roughly the ratio of the transition temperatures.

### 3.1.7. V-Pt

Blaugher *et al.*<sup>29</sup> report  $T_c = 2.53$  K for as-cast A15 phase  $V_3Pt$  and values of 2.86 and 2.61 K for samples annealed at 800°C for 1 h. The  $T_c$  of our as-cast sample is in reasonable agreement with their value, but has the significantly higher value of 3.18 K following an 800°C anneal for 2 days. This value of  $T_c$  has been observed<sup>23,29</sup> for samples annealed for several days at  $\sim 1100^\circ\text{C}$ , for which Blaugher *et al.*<sup>29</sup> report a lower degree of order than in a sample which had been annealed at 800°C.

The pressure dependence of  $T_c$  is found to have doubled after annealing the as-cast sample.

### 3.1.8. V-Ir

The A.15 structure in the V-Ir system has been reported<sup>30</sup> to be stable from 25 to 39 at. % Ir.  $V_3Ir$  has been reported normal to 0.015 K, but samples containing 31, 33, and 37 at. % Ir have  $T_c$  values of 0.91, 1.39, and 1.71 K, respectively.<sup>1,23</sup> The transition curve for our as-cast sample containing 33 at. % Ir is broad and exhibits structure which suggests that there were two overlapping transition centered about 1.6 K.

## 3.2. Niobium

### 3.2.1. Nb-Sn

The  $Nb_3Sn$  sample studied was a piece of sintered material prepared at RCA, and it had a sharp transition at 17.832 K.

There have been a number of previous determinations<sup>18,20,31-33</sup> of the pressure dependence of  $T_c$  for  $Nb_3Sn$  with the various sets of data falling on one of two lines represented by  $\partial T_c / \partial P = -1.3 \times 10^{-5} \text{ K}\cdot\text{bar}^{-1}$  and  $-9.6 \times 10^{-5} \text{ K}\cdot\text{bar}^{-1}$ , with the present data closely following the lower value. An examination of the experimental techniques employed in the various determinations reveals that the data represented by the smaller pressure dependence were taken using fluid pressure transmitting media, whereas considerably less hydrostatic pressure techniques had been used in the other measurements.  $Nb_3Sn$ , like  $V_3Si$ , exhibits a considerable anisotropy in its uniaxial stress dependence of  $T_c$ <sup>35</sup> and therefore a deviation from hydrostatic pressure conditions will considerably influence the observed pressure dependence. It is interesting to note that the measurements of Itskevich *et al.*<sup>32</sup> exhibit a negative deviation from linearity above  $\sim 8$  kbar, which is around the pressure at which their oil-kerosene pressure medium would freeze at room temperature.

The discontinuity in the volume thermal expansion at  $T_c$  for  $Nb_3Sn$  has been determined to be  $4.5 \times 10^{-7} \text{ deg}^{-1}$  by Lazarev *et al.*<sup>34</sup> Substituting

this value and  $6.32 \times 10^5 \text{ erg}\cdot\text{cm}^{-3}\cdot\text{deg}^{-1}$  for the corresponding discontinuity in the heat capacity<sup>35</sup> into

$$\partial T_c / \partial P = T_c (\alpha_n - \alpha_s) / (C_n - C_s)$$

we obtain  $\partial T_c / \partial P \sim -1.3 \times 10^{-5} \text{ K}\cdot\text{bar}^{-1}$ , in good agreement with the directly determined hydrostatic pressure value.

### 3.2.2. Nb-Al

No measurements on  $\text{Nb}_3\text{Al}$  were made in the present investigation. However, for completeness data taken from the measurements of Naubauer<sup>20</sup> are included in Table I.

### 3.2.3. Nb-Ge

Matthias *et al.*<sup>36</sup> report that stoichiometric  $\text{Nb}_3\text{Ge}$  can only be obtained from the melt by rapid quenching and has a  $T_c$  around 17 K. They find that for normal cooling rates an as-cast sample has  $T_c = 6.9 \text{ K}$ . Our as-cast sample has a sharp transition at 6.281 K.

It is interesting to note that although rapid quenching from the melt results in a decreased lattice parameter and a substantially higher  $T_c$  value for  $\text{Nb}_3\text{Ge}$ , compression of as-cast material results in a depression of  $T_c$ . Thus, it would appear that the lattice volume is not the deciding factor for the value of  $T_c$ , which supports the contention of Matthias *et al.* that it is the stoichiometry which dictates  $T_c$ .

### 3.2.4. Nb-Al-Ge

A sample of composition  $\text{Nb}_{0.78}(\text{Al}_{0.75}\text{Ge}_{0.25})_{0.22}$  was obtained from the Bell Telephone Laboratories. The transition to the superconducting state is widespread, but the onset at 20.29 K is reasonably sharp and the pressure dependence of  $T_c$  has been determined relative to it. The present value for  $\partial T_c / \partial P$  is almost an order of magnitude smaller than that reported<sup>20</sup> by Neubauer for several as-cast  $\text{Nb}_3(\text{Al}, \text{Ge})$  ternary samples having  $T_c$  values  $\sim 18 \text{ K}$ .

### 3.2.5. Nb-Ga

Our as-cast sample of  $\text{Nb}_3\text{Ga}$  has  $T_c = 14.54 \text{ K}$ , in agreement with the published<sup>1</sup> value for the A15 phase compound.

### 3.2.6. Nb-Au

Blaugher *et al.*<sup>29</sup> report an as-cast sample of  $\text{Nb}_3\text{Au}$  to be completely in the A15 phase. A number of values for  $T_c$  have been reported<sup>1,23,29,37</sup> ranging from 8.99 to 11.5 K for as-cast samples. Increases of the lower  $T_c$  values to  $\sim 11 \text{ K}$  were achieved<sup>29,37</sup> by annealing at 700–800°C. Our as-cast sample had  $T_c = 11.076 \text{ K}$ , and annealing at 780°C for 12 days produced

only a modest increase of  $T_c$  and a slight enhancement of the pressure dependence.

### 3.2.7. Nb-Ir

Our as-cast sample of Nb<sub>3</sub>Ir has a  $T_c$  of 2.07 K, which is somewhat higher than previously reported<sup>1,23,29</sup> values ( $\sim 1.7$  K). The transition curve is relatively broad and shows evidence of structure suggesting more than one transition.

### 3.2.8. Nb-Rh

The transition onset for our as-cast Nb<sub>3</sub>Rh sample is very sharp with approximately 60% of the transition occurring within 10 mdeg. The  $T_c$  value of 2.797 K is slightly higher than previously reported.<sup>1,23</sup>

### 3.2.9. Nb-Pt

The  $T_c$  of 8.111 K for our as-cast sample is in very good agreement with values quoted by Flükiger *et al.*<sup>37</sup> and Blaughner *et al.*<sup>29</sup> Annealing the sample at 800°C for 1 day produced a slight increase of  $T_c$  and a sharpening of the transition. Pressure measurements were not made for this sample condition. The sample was then further annealed at 900°C for 10 days after which the transition has broadened considerably and now has a sharp onset at 10.53 K. Heat capacity measurements by Spitzli<sup>23</sup> on a sample subjected to a similar heat treatment indicate that only a portion of the sample becomes superconducting at this higher temperature and the remainder retains its as-cast  $T_c$  value. There were clear indications of a double transition in the present measurements, but both were above 10 K and no evidence of any further transition around 8 K was found. Pressure measurements for the annealed sample were made relative to the transition onset, revealing a dramatic change in the pressure dependence of  $T_c$  from the negative dependence observed in the as-cast state to a positive dependence. Furthermore, a strong negative departure from linearity occurs above 10 kbar and the variation of  $T_c$  up to 25 kbar may be represented by

$$\Delta T_c = 1.88 \times 10^{-5} P - 0.03 \times 10^{-8} P^2$$

where  $P$  is the pressure in kbar.

## 3.3. Tantalum

### 3.3.1. Ta-Sn

Our sample of Ta<sub>3</sub>Sn was prepared by sintering. The powdered constituents were pressed into a pellet at a pressure of  $\sim 5$  kbar, sealed in a quartz tube and reacted at 650°C for 1 day. The reacted material was then ground up, repressed to 5 kbar, sealed into a quartz tube, and annealed

for 5 h at 1200°C. On removing the sample a small quantity of free tin was found in the bottom of the tube which would suggest that the sample may be slightly tin deficient. This may account for the slightly lower  $T_c$  value of 5.82 K compared with previously reported<sup>24,25</sup> values of 6.0 and 6.4 K.

### 3.4. Titanium

#### 3.4.1. Ti-Sb

Our as-cast sample of Ti<sub>3</sub>Sb has  $T_c = 5.10$  K, in good agreement with the value of 5.0 K determined from heat capacity measurements<sup>38</sup> on an A15 phase sample by Junod *et al.* Annealing for 36 h at 800°C raised  $T_c$  to 5.47 K and changed the pressure dependence from being weakly negative to positive. Junod *et al.* report a somewhat greater increase of  $T_c$  for a 5-day anneal at 850°C.

#### 3.4.2. Ti-Ir

The sample of Ti<sub>3</sub>Ir examined was received in the annealed state, and therefore measurements could not be made in the as-cast condition. This sample had been annealed at 1000°C for 1 day and 600°C for 2 weeks and has  $T_c = 4.970$  K, which is somewhat higher than the 4.63 K reported by Blaugher *et al.*<sup>29</sup> for a sample annealed at 800°C for 1 h.

### 3.5. Molybdenum

#### 3.5.1. Mo-Si

Our as-cast Mo<sub>3</sub>Si sample has  $T_c = 1.402$  K, compared with a previously reported<sup>1</sup> value of 1.3 K.

#### 3.5.2. Mo-Ge

Two as-cast samples of Mo<sub>3</sub>Ge were prepared. One sample has  $T_c = 2.166$  K, which is considerably higher than the previously reported<sup>1</sup> value of 1.43 K. However, it was noted that the weight loss on preparation was abnormally high for this sample, and assuming that it is entirely due to the loss of Ge the adjusted composition would be Mo<sub>3.1</sub>Ge. The other sample, for which there was negligible weight loss during preparation, has  $T_c = 1.600$  K, in closer agreement with the previously published value. This behavior would suggest a strong compositional dependence of  $T_c$  for the A15 phase around Mo<sub>3</sub>Ge similar to that found<sup>29</sup> for many of the A15 compounds. No significant difference in the pressure dependence of  $T_c$  for the two compounds could be distinguished.

#### 3.5.3. Mo-Os

The compound Mo<sub>3</sub>Os is of particular interest. In the as-cast condition it forms as a two-phase mixture of the bcc Mo and the  $\sigma$  phase structures

and has  $T_c \sim 6.8$  K.<sup>39</sup> The superconductivity is assumed to be associated with the  $\sigma$  phase, which was originally mistaken for the A15 phase, judging from the earlier reported<sup>1</sup>  $T_c$  of 7.2 K. On heating to  $\sim 1200^\circ\text{C}$  there is a transformation to the A15 phase, which is then stable on cooling to lower temperatures.<sup>39</sup> Two A15 phase  $\text{Mo}_3\text{Os}$  samples were obtained which had been prepared by slightly different heat treatments, the main difference being in the final annealing temperature. A sample held at  $1800^\circ\text{C}$  for 2 h and then annealed for 2 weeks at  $600^\circ\text{C}$  had  $T_c = 11.69$  K, while a second sample heated to  $2000^\circ\text{C}$  for 2 h and then annealed at  $1000^\circ\text{C}$  for 2 weeks had  $T_c = 12.50$  K. These values may be compared with the  $T_c$  of 11.68 K reported by Blaugher *et al.*<sup>29</sup> for an A15 phase sample formed at  $2000^\circ\text{C}$ . Both samples followed the same pressure dependence of  $T_c$ .

Pressure measurements were also made on a  $\sigma$  phase  $\text{Mo}_3\text{Os}$  sample<sup>39</sup> having  $T_c = 6.824$  K from which  $\partial T_c / \partial P = -0.57 \pm 0.04 \times 10^{-5} \text{ K}\cdot\text{bar}^{-1}$ .

#### 3.5.4. Mo-Ir

The sample of  $\text{Mo}_3\text{Ir}$  studied was received after being heat treated at  $1800^\circ\text{C}$  for 2 h and then annealed for 2 weeks at  $600^\circ\text{C}$  and has a  $T_c$  of 8.174 K, in good agreement with previously reported<sup>1,29</sup> values for the A15 phase.

### 3.6. Chromium

#### 3.6.1. Cr-Ru

Blaugher *et al.*<sup>29</sup> report that the alloy of composition  $\text{Cr}_3\text{Ru}$  which they examined was not single phase, but that a single-phase A15 compound was obtained at the composition  $\text{Cr}_{0.72}\text{Ru}_{0.28}$ . The sample which we studied was received after being annealed at  $900^\circ\text{C}$  for 1 month and has a very sharp transition at 3.468 K, in good agreement with the values of 3.43 and 3.42 K reported<sup>23,29</sup> for samples annealed for a similar period at  $800^\circ\text{C}$ .

#### 3.6.2. Cr-Os

Blaugher *et al.*<sup>29</sup> report that the as-cast alloy of composition  $\text{Cr}_3\text{Os}$  is two phase containing the body-centered cubic chromium solid solution and the  $\sigma$  phase, but the A15 phase is obtained at the composition  $\text{Cr}_{0.72}\text{Os}_{0.28}$  after heat treating for 24 h at  $1400^\circ\text{C}$ . A slow-cooled sample had a  $T_c = 4.03$  K, whereas for a fast-cooled sample  $T_c = 3.86$  K. Spitzli<sup>23</sup> reports a  $T_c$  of 4.25 K for a sample annealed at  $1000^\circ\text{C}$  for 2 weeks. Our sample, which was annealed at  $1200^\circ\text{C}$  for 1 day and then fast cooled by quenching into water, has  $T_c = 3.862$  K.

## 4. DISCUSSION

### 4.1. Correlations of $T_c$ with Volume

The intensive study of the A15 phase compounds has undoubtedly been motivated by the high transition temperatures which occur for this structure. The complexity of the problem of predicting a prescription for a high  $T_c$  material places it beyond the abilities of present theoretical approaches, and advances towards higher transition temperatures have been made by purely empirical methods. A number of attempts, enjoying varying degrees of success, have been made to find some correlation between  $T_c$  and some simple, normal state parameter in the wealth of data for binary and ternary A15 systems. Many of these correlations have involved modifications of Matthias' electron-per-atom ( $e/a$ ) rule,<sup>3</sup> principally to include the lattice volume. While such correlations may provide a useful guide to higher  $T_c$  values, particularly in the choice of complex compositions, it does not necessarily follow that the apparent volume dependence has any real physical significance. This is illustrated by the system  $V_3Ge_{1-x}Al_x$ , mentioned above, where the substitution of Al for Ge expands the lattice and strongly enhances  $T_c$ , yet compressing the lattice by the application of pressure does not reverse the process, but actually increases  $T_c$  further. We shall consider some further examples of such correlations incorporating the volume and examine to what extent the correlation holds for changes of  $T_c$  produced under pressure.

Zegler<sup>41</sup> noted that those compounds which have the largest cell volume at a given  $e/a$  for a number of ternary compounds based on  $Nb_3Rh$  have the lowest  $T_c$ . He further found that it was possible to express the variation of  $T_c$  in the different systems by a simple linear function of the change of  $e/a$  ( $\Delta N$ ) and the cell volume ( $\Delta V$ ), i.e.,

$$\Delta T_c = a\Delta N - b\Delta V$$

However, if we apply such a relationship to the application of pressure to  $Nb_3Rh$ ,  $\Delta V$  will be negative,  $\Delta N$  zero, and a positive pressure dependence for  $T_c$  is predicted, which, unfortunately is contrary to that which is observed.

Cody *et al.*<sup>24</sup> arrive at the empirical expression

$$T_c(M, V) = T_{c0}(M_0, V_0)(M_0/M)^3 \exp 0.12(V - V_0)$$

to describe the variation of  $T_c$  over the system  $(Nb, V, Ta)_3Sn$ , in which the values of  $T_{c0}$ ,  $M_0$  (atomic mass), and  $V_0$  corresponding to the compound  $NbVTaSn$  were substituted. This relationship predicts that  $T_c$  would always decrease under pressure for the compounds in this system, thus putting it in conflict with the observed increase for  $V_3Sn$ .

Roberts<sup>2</sup> has pointed out that if  $T_c$  is plotted against the valence electron density the data for the Nb- and V-based A15 compounds fall under two sharply peaked envelopes centered at electron densities of  $\sim 0.27$  and  $\sim 0.35$  electrons/ $\text{\AA}^3$ . This correlation for the compounds studied in the present investigation is demonstrated in Fig. 2. Thus, we might expect that any compound lying to the left of the appropriate optimum electron density would exhibit an increase of  $T_c$  under pressure and a decrease if it is situated on the right. A comparison of the data in Table I with Fig. 1 reveals a certain degree of agreement for the V-based compounds, but the overall correspondence is rather poor. Furthermore, Müller<sup>16</sup> has pointed out that the correlation of  $T_c$  with electron density is not followed very satisfactorily when applied to a number of ternary systems.

The latter observation led Müller<sup>16</sup> to suggest the application of the optimized distance correlation of Pessall and Hulm<sup>5</sup> to the A15 compounds. In this approach, which was originally formulated for the superconducting interstitial compounds, the importance of the lattice volume in determining  $T_c$ , as represented by an optimum atomic separation, is inferred from a plot of  $T_c$  against the ratio  $R$  of the lattice parameter calculated from the Goldschmidt radii of the component atoms, to that observed. In the case of the  $V_3X$  compounds the data roughly lie on a single peak where  $V_3Au$ ,  $V_3Pt$ , and  $V_3Ga$  have  $R < R_{opt}$  and  $V_3Sn$ ,  $V_3Si$ , and  $V_3Ge$  have  $R > R_{opt}$ ,

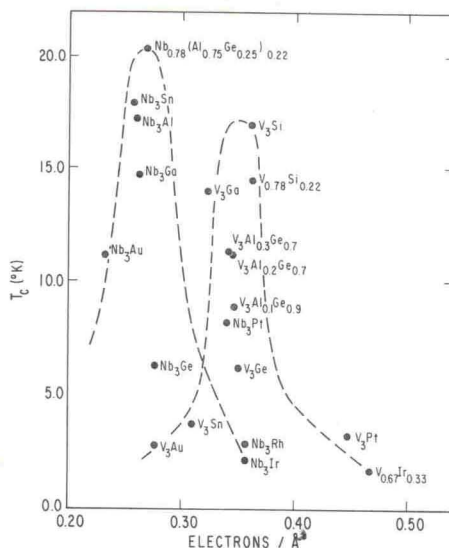


Fig. 2. Correlation plot of  $T_c$  with electron density for the  $V_3X$  and  $Nb_3X$  compounds studied under pressure.

where  $R_{\text{opt}} \sim 1.02$  is the optimum value of  $R$  for a high  $T_c$  value. Thus, since  $R \propto 1/a$  we might expect the former group of compounds to have positive pressure dependences and the latter negative. However, again there is no convincing degree of agreement between the sign of the observed pressure dependence and that predicted. A similar situation is found for the  $\text{Nb}_3\text{X}$  compounds.

#### 4.2. Theoretical Approaches to $T_c$

The basic explanation of superconductivity was provided over a decade ago by the BCS theory,<sup>42</sup> which leads to the general relationship

$$kT_c \sim \hbar\omega \exp(-1/g) \quad (1)$$

for an attractive interaction of strength  $g$  and characteristic energy  $\hbar\omega$  acting between an electron pair. In the BCS formalism the attractive interaction is a consequence of the coupling of the electrons to the lattice vibration—the electron–phonon model—and  $\hbar\omega \sim k\theta_D$  and  $g = N(0)V$ , where  $N(0)$  is the electron density of states at the Fermi level and  $V$  is some average attractive electron–electron interaction parameter. Numerous extensions to this theory have been made improving the sophistication of the model, but the basic form of (1) is retained. A widely used expression for  $T_c$  is that derived by McMillan<sup>43</sup> for a model phonon spectrum, based on that for niobium. This has the form

$$T_c = (\theta_D/1.45) \exp \{ -1.04(1 + \lambda)/[\lambda - \mu^*(1 + 0.62\lambda)] \} \quad (2)$$

where the electron–phonon interaction parameter  $\lambda$  is related to the electron mass renormalization by

$$m^* = m_b(1 + \lambda) \quad (3)$$

$m_b$  being the band mass as derived from a band structure calculation. The parameter  $\mu^*$  is a measure of the direct repulsive electron–electron interaction and is related to the screen Coulomb potential  $V_c$  by the relationship

$$\mu^* = N(0)V_c/[1 + N(0)V_c \ln(E_f/\theta_D)] \quad (4)$$

Values for  $\mu^*$  may be derived for a number of superconductors from the isotopic mass dependence of the transition temperature  $T_c \propto M^{-\alpha}$ , where

$$\alpha = \frac{1}{2} \{ 1 - [\mu^* \ln(\theta_D/1.45T_c)]^2 / [(1 + 0.62\lambda)/(1 + \lambda)] \} \quad (5)$$

Since  $\mu^*$  is expected to vary more slowly than  $1/k_f$  (i.e.,  $< V^{1/3}$ ) in the free-electron approximation, it is usually taken to be independent of pressure. This assumption presents no difficulties for the nontransition metals, but it is not so evident that it will be valid for the transition metals.

A full treatment of the problem of calculating  $\lambda$  requires a detailed knowledge of the phonon and electron spectra, along with the appropriate electron-ion matrix elements. Such calculations have only just been realized<sup>44</sup> for the nontransition metals using the pseudopotential approximation, where the appropriate pseudopotential and pseudo-wave functions describing the interaction of the electron and the ion are taken from fits to the measured Fermi surface. A direct calculation of  $\lambda$  for the transition metals and their alloys would be a considerable undertaking and has yet to be attempted. A number of model calculations have been offered,<sup>43,45,46</sup> all of which lead to the general form

$$\lambda = C/M\langle\omega^2\rangle \quad (6)$$

with the major differences being associated with the physical significance of the parameter  $C$ , which is directly related to the electron-ion interaction. McMillan<sup>43</sup> empirically demonstrated that  $C = N(0)\langle I^2 \rangle$ , where  $\langle I^2 \rangle$  is the mean of the square of the electron-ion interaction, was roughly constant (at least for the bcc transition elements). It has also been generally assumed that  $C$  will be volume independent, though it is not at all clear why this should be so. Hopfield<sup>45</sup> has related  $C$  to the product of the gradient of the atomic potential in the overlap region and the  $p$ -like density of states, and therefore describes  $C$  as being an atomic-like property of the transition metal atom. Barišić, Labbé, and Friedel<sup>46</sup> have considered the phonon induced  $d$ - $d$  coupling within the tight-binding approach and relate  $\langle I^2 \rangle$  to the spread of the  $d$  wave function which they express as  $\sim e^{-q_0 a}$ , where  $q_0$  is the Slater coefficient and  $a$  is the atomic separation.

We may now examine to what extent these various models are able to provide some insight into the expected pressure dependence of  $T_c$ . As may be seen from Table I,  $T_c$  may increase or decrease, with as much as an order of magnitude variation in the size of the effect, under the application of pressure. Similar behavior is found for the transition elements themselves. While it would be too much to expect quantitative agreement between experiment and theory, at its present level, it could be at least hoped that the general trend would be evident, i.e., whether  $T_c$  would increase or decrease.

Clearly, from (2) and (6), if we take  $\mu^*$  to be constant, then it would be impossible to have  $T_c$  increasing under pressure if  $C$  were constant, unless there was a pressure-induced softening of the lattice, which is considered to be highly unlikely. (Strictly, the stiffening of the lattice resulting in an increase of  $\theta_D$  could lead to an increase of  $T_c$ , but this effect is expected to be small.) The question then is whether  $C$  can increase with a decrease of volume and whether the change can be sufficient to compensate for the shift in the phonon spectrum.

In the application of his model to the A15 compounds Hopfield notes that an enhancement of  $C$  by a factor of 1.77 over that for the transition element alone yields reasonable calculated values for the transition temperature for a number of the  $V_3X$  and  $Nb_3X$  compounds. Furthermore, it is the approximately 15% smaller atomic volume of the transition metal in these compounds which is suggested to be the reason for the enhancement. Interpreting this literally as a positive pressure dependence for  $C$  we have  $\partial \ln C / \partial \ln V \sim -5.1$ . From (6)

$$\partial \ln \lambda / \partial \ln V = (\partial \ln C / \partial \ln V) + (\partial \ln \langle \omega^2 \rangle / \partial \ln V) \approx (\partial \ln C / \partial \ln V) + 2\gamma_G \quad (7)$$

Thus, providing  $\gamma_G$  is not greatly larger than the normal value of  $\sim 1.5$ ,  $\lambda$  and hence  $T_c$  could be expected to increase with decreasing volume. Unfortunately, this prediction would be equally true for all of the  $V_3X$  and  $Nb_3X$  compounds and does not allow for the negative dependences that are observed, particularly in the latter group.

Turning to the McMillan formalism we may argue that since the application of pressure will broaden the energy bands the screening will be reduced and  $\langle I^2 \rangle$  will increase, but at the same time  $N(0)$  will decrease. Thus, it is not immediately clear what the net dependence for  $C$  will be. If we adopt the tight-binding approximation proposed by Barišić *et al.* we may rewrite (6) as

$$\lambda \propto W^{-1} W^2 / M \langle \omega^2 \rangle \quad (8)$$

where the band width  $W$  is proportional to the spread to the  $d$  wave function,  $e^{-q_0 a}$ . Thus, we may rewrite (7) replacing  $C$  by  $W$ . Since  $\delta W / W = -q_0 a (\delta a / a) = -q_0 a \delta V / 3V$  we have  $\partial \ln W / \partial \ln V = -q_0 a / 3$ . Typically,  $q_0 \sim 1 \text{ \AA}^{-1}$  and  $a \sim 3 \text{ \AA}$ , thus  $\partial \ln W / \partial \ln V \sim -1$ , which has to be compared with  $2\gamma_G$ , a quantity of opposite sign and, in general, of order two to three times this value. Thus, we see from this simple calculation that the effect of the shift in the phonon spectrum is expected to dominate and will always lead to the prediction of a negative pressure dependence for  $T_c$ .

We may attempt to overcome the above difficulties by invoking the appropriate volume dependence for  $\mu^*$ . A sufficient decrease of  $\mu^*$  has been previously suggested<sup>57</sup> as a possible source of the positive pressure dependence of  $T_c$  which is observed for a number of the early transition metals. This possibility may be investigated, in principle, by a determination of the pressure dependence of the isotope effect, but as yet this has not been attempted. Thus, in the absence of any direct supporting evidence, the adoption of such a procedure in a calculation of  $\partial T_c / \partial P$  would be <sup>no</sup> more than an *ad hoc* assumption designed to provide the correct answer.

An intriguing feature of the controversy which surrounds the entire question of superconductivity in the transition metals and their alloys is the possibility of an alternative attractive interaction to that acting through the phonons being responsible for the formation of the electron pairs. Some very interesting and at times quite exotic interactions have been proposed.<sup>47,48</sup> Unfortunately, for the most part the formalism is too vague to permit any direct comparison with experiment. However, Fröhlich<sup>48</sup> has pointed out the possibility of an attractive interaction between the electrons due to the shielding of the motion of the unfilled *d*-band electrons by the *s* electrons. This idea has been extensively examined by Rothwarf,<sup>49</sup> who has attempted to explain a number of the features of the normal and superconducting state properties of the transition metals and their alloys with this model. Unfortunately, the number of parameters in the expression for  $T_c$  which can vary with the volume again prevents any definite prediction of even the sign of the pressure dependence.

The models discussed so far have been of a general nature and may be equally well applied to the transition metals and their alloys. However, models have also been proposed which are designed specifically to describe the variety of unusual normal state properties which are found for many of the A15 compounds (particularly those with high  $T_c$ ), and these lead to expressions for  $T_c$  which differ from that given in (2).

The strong temperature dependence of the magnetic susceptibility for a number of A15 compounds lead Clogston and Jaccarino<sup>50</sup> to suggest the existence of a narrow peak in the density-of-states curve, which the Fermi level intersects. It was subsequently noted by Weger<sup>51</sup> that the orthogonal linear chains of A atoms, which are a feature of the  $A_3B$  A15 structure, give rise to an essentially one-dimensional band structure for the *d* electrons (see Fig. 3). (This will only be true when the B atom is nontransition since mixing of the *d* states from the B atom with the *d* states of the A atom will destroy the one-dimensional character.) Using this model band structure (which is illustrated in Fig. 3) Labbé, Friedel, and coworkers<sup>52</sup> have been able to give a good description of all the unusual normal state properties of the A15 compounds, e.g., the high density of states, the strong temperature dependence of the susceptibility and Knight shift, the elastic behavior, the crystal distortion, etc.

Cohen and coworkers<sup>53</sup> have demonstrated that the essential feature of the Labbé-Friedel model is the proximity of the Fermi level to a sharp, high band edge in the density-of-states curve, and they have been equally successful in accounting for the normal state properties using the considerably simpler density-of-states model which is also shown in Fig. 3. Thus, in so far as the normal state properties are concerned the two model approaches provide very similar results.

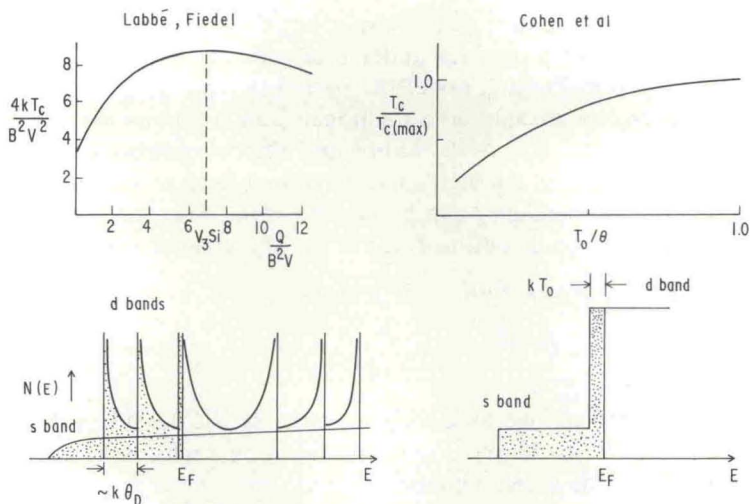


Fig. 3. Schematic representation of model energy bands and dependence of  $T_c$  on  $d$ -band occupation for A15 compounds.

When we come to consider the superconducting state the predictions of the two models differ quite considerably. In the Labbé-Friedel model the narrowness of the  $d$  band places the limits on the energy range of the pairing interaction and not, as is usually the case, the width of the phonon spectrum. This removes the normal exponential dependence of  $T_c$  on the strength of the pairing interaction. Labbé, Barišić, and Friedel<sup>54</sup> have related  $T_c$  to the parameters of the model with the plot in Fig. 3, where  $Q$  is the number of electrons in the band,  $V$  is the electron coupling  $[= \lambda/N(0)]$ , and  $B$  is a renormalization constant related to the band structure.

In the Cohen model the range of the interaction is only restricted at low energies, and therefore the effect on the form of the relationship for  $T_c$  is less pronounced. For the energy-band scheme illustrated in Fig. 3 (which is that appropriate to the cubic case)  $T_c$  is given by the relationship

$$T_c = 1.13(\theta_D T_0)^{1/2} \exp [-(1 + \frac{1}{2}\lambda)/(\lambda - \mu^*)] \quad (9)$$

for  $\theta_D \gg T_0 \gg T_c$ , where  $kT_0$  is the Fermi energy relative to the band edge. The variation of  $T_c$  with  $T_0$  for a fixed value of  $\lambda$  is shown schematically in Fig. 3.

We see that from the point of view of the pressure dependence of  $T_c$  the problem is now further complicated by the possibility of interband transfer strongly influencing  $T_c$ , particularly at low band occupations, in addition to the difficulties associated with the pressure dependence of the pairing interaction which have already been discussed. The possibility

of a change of band occupation could be investigated by measurements of the normal state properties under pressure.

In the Labbé-Friedel model the particular case of  $Q/B^2V \sim 7$  places  $T_c$  close to its maximum value as a function of  $Q$  and results in the considerably simpler expression  $kT_c \approx B^2V^2$ . Labbé and Friedel estimate that this is the condition for  $V_3Si$  and Barišić<sup>55</sup> has argued that the sign and the magnitude of the pressure dependence can be derived from this expression using the tight-binding approach outlined above for the general case. Thus,

$$V = \lambda/N(0) = \langle I^2 \rangle / M \langle \omega^2 \rangle \propto W^2 / \langle \omega^2 \rangle \quad (10)$$

$$\text{As } B^2 \propto W^{-1}$$

$$T_c \propto W^3 / \langle \omega^2 \rangle^2 \quad (11)$$

In estimating the change of  $T_c$  with pressure Barišić considers the increase in the band width to be the dominant effect and neglects the effect due to the stiffening of the lattice vibrations. Thus,

$$\delta T_c / T_c = 3\delta W / W = -q_0 a (\delta V / V) \sim -2.4 (\delta V / V)$$

since with  $q_0 \sim 1 \text{ \AA}$ ,  $q_0 a \sim 2.4$ . With a bulk modulus of 1760 kbar  $\delta V / V$  at 25 kbar is  $-1.4\%$ , and hence the estimated value for  $\delta T_c / T_c$  is  $\sim 3.4\%$ , which compares quite favorably with the measured value of  $5.4\%$ . However, if we make the simplest assumption regarding the effect of the change in the phonon frequencies, namely,

$$\delta \langle \omega^2 \rangle^2 / \langle \omega^2 \rangle^2 = 4(\delta \omega / \omega) = 4\gamma_G (\delta V / V)$$

and assume that  $\gamma_G \sim 1$ , then the estimated fractional change of  $T_c$  is now  $\sim -2.2\%$ .

The measurement of the pressure dependence is intrinsically a stringent test of any theoretical expression for  $T_c$  and the present measurements do not favor any particular one of the prevailing models, all of which are equal in the inadequacy of their description of the pressure dependence.

#### 4.3. Influence of Ordering

The influence of the degree of atomic order on  $T_c$  has been conclusively demonstrated<sup>29</sup> for a number of A15 compounds, with  $V_3Au$  undoubtedly being the most outstanding example. For the most part an increase of the atomic order results in an increase of  $T_c$ . This behavior has been offered as evidence in support of the linear chain model, where it is important to avoid the disruption of the A atom chains if the highest  $T_c$  is to be obtained.<sup>56</sup> While such an argument may be applicable to those compounds which are formed with a nontransition metal, where the  $d$  character of the energy bands will be dictated by the atoms in the linear chains, it is not clear that

it is at all appropriate where both are transition metals. Yet effects of ordering on  $T_c$  are also observed for these compounds. From an extensive study of the low-temperature heat capacity of a large number of A15 compounds Spitzli<sup>23</sup> has been able to demonstrate that ordering effects the density of states in the same sense as  $T_c$ .

In addition to influencing  $T_c$ , the degree of order also effects its variation with pressure, even in certain cases to the extent of changing the sign of the effect. For  $V_3Au$ ,  $V_3Si$  (where the differences between  $V_3Si$  and  $V_{0.78}Si_{0.22}$  are considered to be largely due to the disordering of the vanadium chains), and  $Nb_3Au$ ,  $\partial \ln T_c / \partial P$  is found to be essentially constant, i.e.,  $\partial T_c(P) / \partial P \propto T_c(0)$ . Thus, the effects of ordering and the application of pressure on  $T_c$  for these compounds may be regarded as being in effect equivalent, and the data for any particular compound may be represented by the simple linear relationship

$$T_c(P)/T_c(P_0) = 1 + a(P + P_0)$$

where the effective "zero pressure"  $P_0$  is determined by the degree of order. This equivalence suggests that the major factor in the change of the transition temperature is a shift of the Fermi energy, presumably to a region of higher density of states, without any appreciable change in the shape of the energy bands. No simple explanation can be offered for the variation in pressure dependence with order observed for  $V_3Pt$ ,  $Nb_3Pt$ , and  $Ti_3Sb$ , but it seems likely that here changes in the band structure will be involved. It may be noted that  $\partial \ln T_c / \partial P$  is roughly the same for  $Mo_3Os$  whether it has the A15 or the sigma-phase structure.

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