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### Publication Date

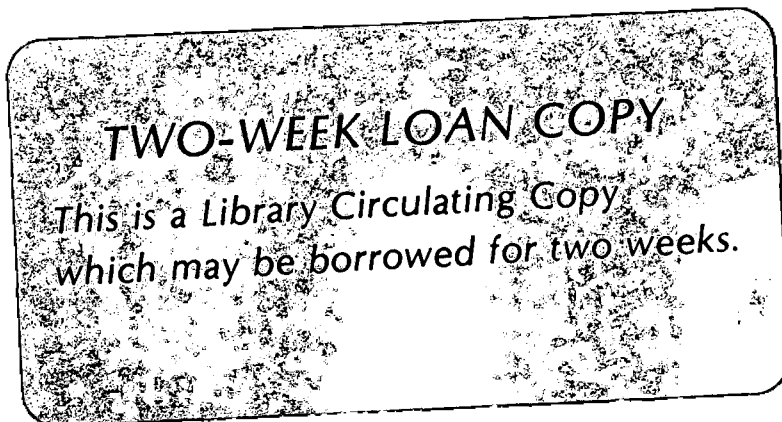
1970-12-01

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December 1970

AEC Contract No. W-7405-eng-48



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UCRL-20381

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THE SYNTHESIS OF LOW TEMPERATURE PHASES BY THE CO-CONDENSATION  
OF THE ELEMENTS: A NEW SUPERCONDUCTING A15 COMPOUND,  $V_3Al$ .\*

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A method is described whereby intermetallic phases which are not stable at high temperatures may be formed using controlled vacuum evaporation of the elements.  $V_3Al$  with the A15 structure was formed on substrates held at temperatures below 350°C. For the as-deposited sample the lattice parameter was 0.483 nm and the superconducting critical temperature was 8.5°K.

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\* Research supported by the U. S. Atomic Energy Commission.

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In this note we describe a technique which overcomes several difficulties often encountered when conventional metallurgical methods are used to prepare certain combinations of the elements. The application of this technique to the search for new superconductors, in particular the phases with  $Al_5$  (or  $Cr_3Si$ ) structure, is discussed. Finally, we report the synthesis of  $Al_5 V_3 Al$ , for the first time, and our measurements of its lattice parameter and superconducting critical temperature.

Difficulties arise when conventional techniques, such as arc-melting or sintering, are used to combine elements with vastly different properties or when the reactions produce unwanted phases. For example, the maintenance of stoichiometry is a problem with high melting point compounds where one of the elements has a high volatility. In addition, some elements are troublesome in that container materials contaminate the sample. A more basic problem is the retention of a high temperature phase when it is cooled to a temperature below which it becomes metastable with respect to the desired phase. It now appears that some structures of scientific or technological interest are stable only at temperatures so low that the time required for formation is impossibly long.<sup>1</sup>

A method which has the potential to overcome these difficulties is the vacuum evaporation and co-condensation of the elements onto substrates maintained at a controlled temperature. In our work, the individual elements are evaporated from separate sources, usually by electron beam heating. Thus, vapor pressure differences are unimportant. With the localized surface heating provided by electron bombardment, either the element serves as its own crucible or contamination from the crucible is minimized. Contamination from the ambient atmosphere is minimized by

the high evaporation rates possible with electron bombardment. Deposition rates of one micron per minute are typical. The flux of each element is monitored by a chopped-beam ionization type rate monitor and controlled by a feedback loop to the electron beam source. With this technique, the ratio of the elements arriving at the substrate remains constant to within a few percent during the time required to deposit the sample. Thus, the correct composition at a particular place on the substrate is assured. Enhanced atomic mobility due to surface diffusion no doubt aids in establishing equilibrium and homogeneity at relatively low temperatures.

Examples of low temperature stability are found among the phases with the  $A15$  structure. Of 35 systems for which data are readily available,<sup>2,3,4</sup> there are 17 for which the  $A15$  phase is formed by a solid state reaction (i.e. at relatively low temperatures); the rest melt congruently or decompose peritectically. Thus, a number of  $A15$  phases are formed peritectoidally and others, notably  $V_3Ga$ <sup>5</sup> and  $Nb_3Au$ ,<sup>6</sup> are formed from the bcc solid solution as it is cooled. In addition, there are reports of new  $A15$  phases (not included above) having been formed at low temperatures using techniques such as solid state diffusion,<sup>7</sup> low temperature annealing of alloys,<sup>8</sup> and high pressure.<sup>9,10</sup> These techniques require a certain minimum temperature (usually 500-1000°C) in order to achieve reasonable reaction rates. There are still other systems for which electrochemical and size factors<sup>1,11</sup> do not prohibit formation of the  $A15$  phase and yet it has not been observed, even when these low temperature methods are used. An explanation for this may be that the  $A15$  phase in these systems is stable only below these minimum temperatures.

The motivation for searching for new A15 phases is that some of these could have a very high superconducting critical temperature, based on available criteria for high  $T_c$  among the known A15 superconductors.<sup>12</sup> The latter are the most numerous of the high  $T_c$  materials and include  $Nb_3(Al,Ge)$  with a  $T_c$  of 20.7°K, the present maximum.<sup>13</sup> It is by no means certain that this value cannot be exceeded. Therefore, it is desirable to search for new A15 compounds.

The V-Al system is one which should form an A15 phase. Until now, the A15 phase had not been positively identified in numerous experiments which utilized the usual methods mentioned above. This is despite the interest in  $V_3Al$  generated by Matthias, et al., with their announcement of  $Nb_3(Al,Ge)$ , and their prediction that  $V_3Al$  "would be a very high superconductor."<sup>14</sup> Holleck, et al.,<sup>15</sup> claimed to have formed A15  $V_3Al$  with a lattice parameter of 0.492 nm. Several attempts to repeat their results failed.<sup>16,17</sup> It was concluded that Holleck, et al., had formed A15  $V_3Si$  and/or other phases as a result of contamination from the hot pressing in carbon dies or subsequent annealing of their samples in fused quartz ampoules. To check the possibility that carbon, nitrogen or oxygen favors the formation of A15  $V_3Al$ , Müller<sup>18</sup> added C,  $V_2O_5$  and VN to  $V_3Al$  samples. The products observed after heat treatment consisted of carbides and nitrides of vanadium,  $Al_2O_3$ , and the A2 (bcc) V-Al solid solution. The bcc phase exists, in the V-Al system,<sup>19</sup> over an extended range of composition at high temperatures, which is also the case in the V-Ga system. From these considerations, we concluded that A15  $V_3Al$ , if it existed, could only be formed at low temperatures. This idea was recently supported by Müller's work on ternary alloys<sup>18</sup> which suggested

to us that the Al<sub>5</sub> phase would form at about 300°C.

For the purposes of this experiment the substrate (glass or fused quartz) was held at about 350°C. This is the temperature with the shutter closed; the substrate cools somewhat when the shutter is opened. The approximately three micron thick deposits were smooth and of mirror-like quality. The pressure during evaporation was  $3 \times 10^{-7}$  torr.

The use of an extended substrate allows one to make, in a single experiment, a considerable portion of the binary phase diagram. From the x-ray diffraction data of one run, we identified the following in decreasing order of their vanadium content: A2(bcc) solid solution, the Al<sub>5</sub> phase, A2 solid solution again, and the complex cubic phase V<sub>5</sub>Al<sub>8</sub>. These different regions were sometimes apparent visually because of slight differences in reflectance and color. All of the strong diffraction lines expected for Al<sub>5</sub> V<sub>3</sub>Al were observed in the region of the deposit with the composition V<sub>3</sub>Al (as determined both by microprobe and thickness measurements). No extra lines, other than those attributed to the bcc solid solution, were observed.

The lattice parameter of vanadium-rich Al<sub>5</sub> V<sub>3</sub>Al was determined from a powder pattern using material scraped from the substrate. The  $a_0$  was  $0.4830 \pm 0.0003$  nm, near the values of 0.483 to 0.484 predicted on the basis of work on ternary alloys by Müller<sup>18</sup> and Asada, et al.,<sup>20</sup> and in agreement with our prediction of 0.483 nm based on the Geller radii.<sup>11</sup> A slight increase in the lattice parameter with increase in aluminum content indicates that the phase exists over a limited range of composition near 25 atomic percent Al.

It should be noted that both of the substrates used in the work



contain the element silicon. It is possible that  $V_3Si$ , another Al5 phase, could have formed in a very thin layer at the surface of the substrate, and it cannot be ruled out that this could help in the nucleation of the  $V_3Al$  Al5 phase. This will be studied in further work. However, in view of the low temperature, short time (180 sec), and the three micron thickness of the V-Al deposits, it is certain that the bulk of the film was  $V_3Al$  with the Al5 structure, as determined by x-ray measurements. This is also indicated by the fact that the Al5 structure was found only at the  $V_3Al$  composition, between bcc phases.

Thus far, the maximum critical temperature of  $8.5^\circ K$ , as measured resistively, is in approximate agreement with extrapolations from the studies of Otto,<sup>21</sup> and Asada, et al.<sup>20</sup> The extent to which  $T_c$  can be increased by annealing remains to be seen. The critical temperature of Al5 phases is known to be strongly dependent upon the degree of order.<sup>22,23</sup> For example, we prepared  $V_3Ga$  in a similar fashion, with a substrate temperature of  $350^\circ C$ , and the  $T_c$  was  $12.3^\circ K$ , as compared to the value of  $14.5^\circ K$  reported for well annealed samples. Similarly,  $Nb_3Sn$  formed by co-deposition at  $600^\circ C$  had a  $T_c$  of less than  $14^\circ K$ .<sup>24</sup>

In addition to studying the effects of variations in the substrate, substrate temperature, and annealing, we will determine the degree to which  $T_c$  can be increased by alloying.

ACKNOWLEDGMENTS

We wish to acknowledge the help and assistance of the staff at the IMRD, especially Mr. D. Whitaker. We are indebted to Dr. M. Pickus, Messrs. J. Roberts, M. Collver, and R. Loop for assistance and helpful discussions. This work was made possible by the encouragement and support of Professors L. Brewer, E. R. Parker, and V. F. Zackay.

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