On the "Martensitic" Transformation in the A-15 Superconductors Compounds

R. MADAR, J. P. SENATEUR, AND R. FRUCHART

E.R. 155 C.N.R.S.-E.N.S.E.G.P., Domaine Universitaire, 38400—St-Martin-d'heres, France

Although a great number of studies have been reported on the "martensitic" transformation in A-15 superconductors, there are still fundamental questions concerning the nature of the transformation which remain unsolved. After a critical analysis of previous experimental work on this transformation in V_3Si and Nb_3Sn, including our own results, we propose a model for the origin and mechanism of the tetragonal distortion based on the consequences of the strong structural relation between the A-15 cubic structure and the W_5Si_3 tetragonal one. As a matter of fact since the analysis of the previous results leads to the conclusion that the transforming A_3B sample has a composition richer in B than stoichiometric, we propose that the distortion is due to a number of defects (antisite type which is larger in transforming than in nontransforming crystals). The presence of these point defects leads to the formation of local strain of tetragonal symmetrical resulting from repulsive interactions between the B atoms, in equilibrium with the cubic symmetry of the three-dimensional network of strongly bonded A atoms. At low temperature, as soon as the lattice softening becomes important enough, a new equilibrium is reached, namely the distortion of the lattice.

Introduction

Since the discovery by Hardy and Hulm (1) of superconductivity at 17°K in V_3Si, the highest T_c material known has continually resided with the A-15 structure compounds A_3B, where A is one of the transition metal Nb or V and B is a metal or a metalloid (e.g., Ga, Si, Ge, Sn).

In addition, these materials frequently possess anomalies in their electrical, magnetic, elastic and structural properties.

In regard to the structural transformation, Batterman and Barrett (2) have been the first to demonstrate that V_3Si and several others β-W structure superconductors undergo second-order transformations from cubic to tetragonal structure at temperature T_m in the range immediately above their supercon-

ducting transition temperature T_c. These authors describe these transitions as "martensitic" in the sense that no diffusion is involved. Since this first paper many experimental and theoretical studies have been published on this phase transition in V_3Si as well as on the similar one in Nb_3Sn at 45°K (3–16).

There are, nevertheless, fundamental questions concerning the nature of the transformation which remains unsolved from both theoretical and experimental points of view.

A feature of the "martensitic" structural transformation in the high-temperature superconductors V_3Si and Nb_3Sn is that the transformation does not take place in all samples of the material and different parts of the same crystal may show different

behavior. The basic difference between the two types of samples has remained a puzzle although a number of explanations, based on deviations from perfect stoichiometry or existence of vacancies, have been suggested (15). The different behavior has been also attributed to the presence of heterophase inclusions in transforming crystals (4, 7, 16, 17) but the microscopically visible amount of second phase did not correlate with the tendency to transform, whereas the electrical resistivity ratio $R_{300°K}/R_{20°K}$ was found to be a relevant measure. The resistance ratio of nontransforming specimens are usually low (about 10) and those of transforming specimens high (up to about 70) (4).

Based on these experimental measurements, Noolandi and Varma proposed that the different type of behavior is due to the larger number of defects in nontransforming than in transforming crystals.

In the present paper, after a critical analysis of the experimental measurements of this "martensitic" transformation in V_3Si and Nb_3Sn including our own results, we propose an hypothesis for the origin and the mechanism of the tetragonal distortion based on the structural similarity between the A-15 cubic structure and the W_5Si_3 tetragonal type. In our model, the transforming sample must have a composition lying the B-rich side of the A_3B phase existence domain, leading to the formation of both antisite substitutional point defects and presence of A_5B_3 phase precipitates along the dislocation lines.

Critical Analysis of the Experimental Measurements on the "Martensitic" Transformation in V_3Si and Nb_3Sn

V_3Si

After Shull (18) observed broadening of the neutron diffraction peaks in V_3Si at temperatures below about 17°K, Batterman and Barrett (2) have studied four single

crystals of V_3Si by X-ray topography methods. They have found that a reversible second-order cubic to tetragonal transformation occurred below a certain temperature T_m. For the different samples, T_m ranged between 23 and 30°K. The value of the c/a ratio at 4.2°K varied from sample to sample, being 1.0025 from the sample which transformed at 30°K.

The X-ray measurements with applied stress of Patel (30) were consistent with the transformation being second-order, as suggested by Anderson and Blount (3).

These observations stimulated elasticity measurement showing a lattice softening on cooling from room temperature to the onset of the martensitic transformation (19, 20). From the whole experimental work on this subject, some important features have to be pointed out:

There is no direct relation between the superconducting behavior and the tetragonal distortion since Batterman and Barrett have found a crystal of V_3Si which remained cubic down to 1.9°K and yet became superconducting below 17°K.

As Greiner and Mason have already reported, single crystals specimens of the transforming phase can contain visible second-phase precipitates, mainly V_5Si_3 up to several percent of the sample (17).

In high-quality single crystals of V_3Si, grown by a floating zone technique, and free of second phase, no tetragonal distortion has been detected at low temperature (11). The same conclusion has been achieved by Kunzler (21) by specific heat measurements on a single crystal of V_3Si which contained no observable amount of a second-phase material

On the other hand, Batterman and Barrett reported, from X-ray observations, that the martensitic transformation cannot be correlated with the amount of second phase present in the crystal. But those samples with high resistivity ratio transformed, whereas those with lower ratio did not.

However we have been able to prepare by the floating zone technique a large single crystal of V_3Si (ϕ 8 mms, $l = 50$ mms) free of second-phase precipitates (22) which did not present a tetragonal distortion at low temperature but with a resistance ratio $R_{300}/R_{20} > 30$ (23).

From these different observations it is clear that the tetragonal distortion is favored by the presence of a given amount of V_5Si_3. From equilibrium considerations we may say that in this case the V_3Si phase has a composition lying on the Si-rich side of the existence domain.

The structural work on this phase has only established that the noncubic phase is in the tetragonal system, but any displacement of the atoms relative to their positions in the cubic phase has not been ascertained. However, Andersson and Blount (3) showed, as a consequence of Landau's theory of second-order phase transformation, that this one cannot be a pure tetragonal strain and that an internal strain parameter might come into play which would manifest itself in a relative displacement of atoms within the unit cell.

Nb_3Sn

Due to the problems encountered in the synthesis of good single crystals of this compound, less studies have been devoted to the "martensitic" transformation in Nb_3Sn than in V_3Si.

First experimental observations of the tetragonal distortion in Nb_3Sn have been reported by Batterman following the discovery of diffraction broadening of powder lines similar to the behavior of V_3Si.

The determination of the lattice parameters at low temperature on single crystals grown by HCl transport technique has shown that Nb_3Sn undergoes a structural transformation at $T_m = 43°K$ from cubic to a tetragonal low-temperature phase with $a > c$: $a/c = 1.0062$ at $4.2°K$.

More recently, a neutron diffraction study of the phase transition in Nb_3Sn (24) by Shirane and Axe has established the presence in Nb_3Sn of sublattice displacement of 12 (+) (D_{4h}^9) type.

However, as in the case of V_3Si, some observations have to be pointed out:

The as-grown crystals used for these experiments showed no sign of structural transformation down to $4.8°K$ but presented a very large lattice softening. It appears that the softening, as for V_3Si, can take place without transformation.

A vacuum treatment of some 20 to 100 hr at $1000°C$ is needed to obtain the transforming crystals.

The transition is of the second-order type since no hysteresis has been detected.

As reported by Hanak most crystals grown by this technique are rich in tin by as much as 30.9 wt% (stoichiometric Nb_3Sn contains 29.7 wt% Sn) and the mass spectrographic analysis of these specimens indicates that the total impurity content ranges between 50 and 250 ppm (excluding hydrogen).

A final remark about these experimental observations is that although indirect evidence has been presented that all high T_c A-15 superconductors undergo lattice transformation (25) the only direct experimental evidence was found in Nb_3Sn and V_3Si.

Structural Relation between the Cubic A-15 (βW) and the tetragonal (D_{4h}^{18}) Type Structures

Since there is some evidence that the presence of the A_5B_3 phase may favor the occurrence of tetragonal distortion in the A_3B phase, we have looked more carefully to the relation between the two structures and its consequences. During the course of our investigation, a more general paper has been published on this subject by Andersson (26) with approximately the same conclusions.

The space group for the cubic A-15 structure is O_h^3, Pm3n, a nonsymmorphic space group. The primitive unit cell is shown in Fig. 1. Each cubic cell contains two A_3B molecules or a total of eight atoms. The two B atoms occupy the body centered cubic positions (a) $(0, 0, 0)$; $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ while the six A atoms are located on the cube faces at the positions 6(d): $(\frac{1}{2}, \pm\frac{1}{4}, 0)$, $(0, \frac{1}{2}, \pm\frac{1}{4})$, $(\pm\frac{1}{4}, 0, \frac{1}{2})$. The A atoms form three sets of orthogonal chains along the x, y, z axes, respectively.

The space group for the tetragonal W_5Si_3 is D_{4h}^{18}, I4/mcm. Each tetragonal unit cell contains four A_5B_3 molecules or a total of 32 atoms in the following positions:

4 A in   4 (b): $(0, \frac{1}{2}, \frac{1}{4})$, $(\frac{1}{2}, 0, \frac{1}{4})$.

16 A in 16 (k):

$$(x_1, y, 0)(\bar{x}_1, \bar{y}, 0)(\bar{y}, x_1, 0)(y, \bar{x}_1, 0)$$

$$(x_1, \bar{y}, \tfrac{1}{2})(\bar{x}_1, y, \tfrac{1}{2})(y, x_1, \tfrac{1}{2})(\bar{y}, \bar{x}_1, \tfrac{1}{2})$$

with

$$x_1 = 0.074, \qquad y = 0.223.$$

4 B in 4 (a): $(0, 0, \frac{1}{4})(0, 0, \frac{3}{4})$

8 B in 8 (h): $(x_2, \frac{1}{2}+x_2, 0)(\bar{x}_2, \frac{1}{2}-x_2, 0)$

$$(\tfrac{1}{2}+x_2, \bar{x}_2, 0)(\tfrac{1}{2}-x_2, x_2, 0)$$
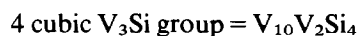
with

$$x_2 = 0.17.$$

As already shown by Andersson, the structure of W_5Si_3 can be accurately derived by means of the Hyde rotation operation (27, 28) on the A-15 tungsten structure.
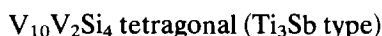
In Fig. 2a the projection of the A-15 structure on the (001) plane is reported as an

array of polygonal cells. If these polygons of atoms are rotated 45° in both directions, as indicated by the arrows, in Fig. 2b, a structure very close to that of V_5Si_3 is obtained. In fact, another path is needed to obtain the true structure of V_5Si_3 which is the partial and ordered substitution of vanadium atoms in the 4 (a) position by silicon atoms as shown on Fig. 2.
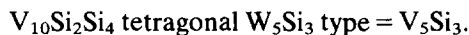
The results of these operations, as far as the composition is concerned, is the following:

4 cubic V_3Si group $= V_{10}V_2Si_4$

rotation:

$V_{10}V_2Si_4$ tetragonal (Ti$_3$Sb type)

substitution:

$V_{10}Si_2Si_4$ tetragonal W_5Si_3 type $= V_5Si_3$.

The origin of the rotation has to be found in a repulsion between silicon atoms since the substituted atoms have four silicon first neighbors and eight vanadium second neighbors in V_3Si whereas in V_5Si_3 they will have eight vanadium first neighbors and four silicon second neighbors.

The main consequences of this very strong structural relation are the following:

In the case of a mixture A_3B and A_5B_3 there must be a simple crystallographic relationship between the grains of the two components to decrease the interfacial free energy. This observation is in agreement with the recent work of Cullis et al. (29) on the T.E.M. analysis of Nb–Ge films. In the case of mixed layers Nb_3Ge–Nb_5Ge_3, most of the Nb_5Ge_3 phase was present as an array of striae resembling closely stacked lamellae, which had regular spacings of 20 Å (twice the parameter of the Nb_5Ge_3 phase and four times the parameter of the Nb_3Ge phase). As suggested by Cullis et al. the lamellae would be twin-related so that the free energy of the Nb_5Ge_3/Nb_3Ge interface would be reduced. Their proposition that the Nb_5Ge_3 can be formed by a martensitic transformation from
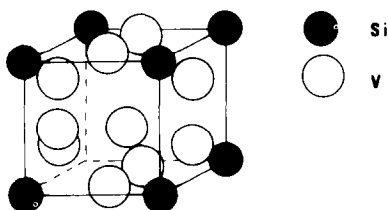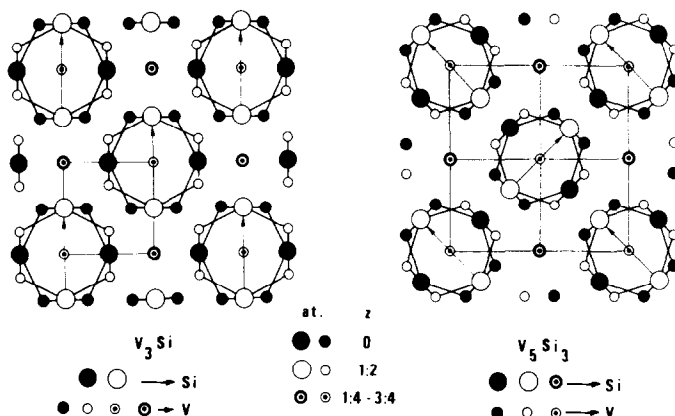

● Si
○ V

FIGURE 1.

FIGURE 2.

Nb_3Ge is not correct since there is a composition change and the twins can be just the result of the strong structural relation between the two structures as reported before.

In the case of an A_3B compound with a composition lying on the B-rich side of the existence domain, we will have some antisite defects consisting in a partial substitution of A by B atoms. These defects leading to a configuration close to the substitution mechanism between the A_3B and A_5B_3 structures would result in a local strain since a clockwise and anticlockwise 45° rotation of the neighbored atoms will be needed to release the repulsive forces. This rotation tendency is opposed by the endless strings of A atoms strongly bonded to each other.

From simple volume considerations the ordered substitution of an A by smaller B atom with rotation of the neighbor atoms (e.g., V_3Si) leads to a reduction of the parameter of the unit cell and as a consequence to a c/a ratio > 1 for the tetragonal cell; the c parameter related to the conservation of the vanadium chain perpendicular to the basal plane is not affected by the transformation mechanism. If however the B atomic radius is larger than that of A (e.g., Nb_3Sn) the resulting c/a ratio will be inferior to 1.

Discussion

The three previous observations constitute the basis of our hypothesis on the origin and mechanism of the tetragonal distortion observed in some A-15 compounds.

We propose that the distortion is due to a larger number of defects (antisite type or precipitation of A_5B_3 along the dislocation lines) in transforming than in nontransforming crystals.

These defects lead to the formation of domains characterized by local strains for tetragonal distortion. On the other hand the cubic symmetry is stabilized by the strong tridimensional network of A–A bonds. This situation can be considered as an equilibrium between two opposite forces:

A strain resulting from the defects which can be released only by the tetragonal distortion;

A force trying to maintain the three-dimensional array of A chains.

At room temperature, the strains are frozen in due to the high stability of the lattice. But at low temperature, as soon as the lattice softening became important enough, a new equilibrium was reached, namely the tetragonal distortion of the lattice.

However, since the superconducting properties, directly related to the conservation of

the A chains, are not affected by the distortion, the displacements of the atoms must be very small. The A sublattice displacements, according to our model, are reported in Fig. 3.

A main consequence of this model is that, for a given lattice softening, the importance of the distortion and also its occurrence (e.g., T_m) is directly related to the value of the strain existing in the crystal or more precisely to the number of point defects (antisite type) and to the cooperative effects of these defects. This observation is in agreement with experimental results showing a wide variation of the importance of the distortion and of the transformation temperature from sample to sample and even for different parts of the same crystal, and also the fact that it is possible to convert nontransforming to transforming samples by annealing (6).

Another advantage of our model is to give a very simple explanation of the difference between the c/a ratio of V_3Si and Nb_3Sn in the tetragonal state based on B/A radius consideration.

From a more theoretical point of view, we may say that this model is in agreement with the predictions of Andersson and Blount on
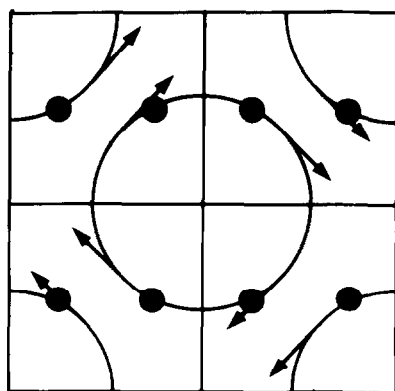
the needed sublattice distortion at the transition and with the "martensitic" character of this transformation since no diffusion of atoms is involved in the proposed process.

Although we cannot exclude that the tetragonal distortion, in the A_3B phase, is induced at low temperature by the presence of A_5B_3 phase along dislocation lines, this other model close to the previous one and based on the same crystallographic considerations, disagrees with the absence of any correlation between the importance of the tetragonal distortion and the amount of A_5B_3 phase present in the crystal as determined experimentally.

Conclusion

After a critical review of the previous experimental and theoretical work on the "martensitic" transformation in A_3B compounds, we propose a model based on the structural relation between the Cr_3Si and W_5Si_3 structures to explain the occurrence of the tetragonal distortion.

The proposed space group for the sublattice displacements given by Shirane and Axe is very close to the D_{4h}^{18} space group of W_5Si_3.

In summary three main features are needed for the tetragonal distortion to occur:
   a B side for the stability domain of the A_3B phase with a composition in B richer than the stoichiometric one;
   the presence of point defects of antisite type in the lattice;
   a cooperative effect of these defects inducing the tetragonal distortion in accordance with the mechanism involved in the Cr_3Si–W_5Si_3 transition.

If these requirements are fulfilled, the value of the c/a ratio must be related to the relative size of the two atoms.

These stringent conditions needed to obtain the transformation may explain why it has been observed only in two of the 70 compounds with the A-15 structure.

$$V_3 S i$$

● V $(z = 0)$

FIGURE 3.

As previously pointed out by Andersson (*26*) the observations made in this article call for experiments with high-resolution electron microscopy in order to reveal whether the ideas proposed are realistic or not. A research program is already started on this subject (*31*).

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