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Mechanisms for a Rapid Phase Transformation of Nb_3Si from the Ti_3P Structure to the Cr_3Si (*A*15) Structure

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Abstract

Nb_3Si in the Cr_3Si (*A*15) structure has been successfully recovered in bulk amounts after shock compressing Nb_3Si in the Ti_3P structure. The material was under compression less than 1 μs. To account for the extreme rapidity of the transformation we find that the essential characteristics of the Cr_3Si structure can be achieved by screw rotating one type of column of Nb-atom pairs 45° and one quarter cell length in the Ti_3P structure. It is further shown that the Fe_3P structure cannot be similarly transformed.

Introduction

We recently recovered bulk amounts of Nb_3Si in the Cr_3Si (*A*15) structure using dynamic high pressures generated by explosives. The lattice parameter is 5·091 ± 0·006 Å, the inductive T_c is 18·6 K, it displays a large specific heat transition at 18·0 K, and has an upper critical field of 12·5 T (Olinger & Newkirk, 1981; Stewart, Olinger & Newkirk, 1981*a*,*b*).

The starting material was prepared by arc melting high-purity niobium and silicon in 3:1 atomic proportions. The alloy was then annealed in vacuum at 2048–2063 K for 3 to 5 h. X-ray powder diffraction measurements on an annealed cylinder showed it to consist primarily of the Ti_3P-type structure. Also, small amounts of Nb_5Si_3 and Nb were present. Preliminary two-dimensional hydrodynamic calculations showed that the bulk of the samples was subjected to a pressure in the range 90 to 110 GPa for less than 1 μs. The temperatures generated in the sample at the peak of the shock were of the order of 1300 K with a residual temperature of about 800 K. The amount of conversion to the Cr_3Si structure was estimated from diffractometer traces to be between 50 to 75% with the residuals composed of Nb, Nb_5Si_3 and some Nb_3Si in the Ti_3P structure.

The phenomenon which prompted this study was the short time interval in which the Ti_3P structure transformed into the Cr_3Si structure. The 100 GPa isobar, for instance, of the shock wave passing through the sample was about 0·8 mm thick and its velocity was 8 mm/μs; thus the material remained above 100 GPa for only about 0·1 μs. It is important to know if such a transformation required diffusion across atomic planes, or required slight shifts in atomic positions. If transformations requiring diffusion could occur in such

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small time intervals, then a large range of structure transformations would be possible.

Discussion

The occurrence of the Ti_3P structure for Nb_3Si was first reported by Rossteutscher & Schubert (1965). They illustrated projections of the Cr_3Si and Ti_3P structures, as well as the similar Fe_3P structure, and a compilation of known alloys in these three structures. The occurrence of Nb_3Si in the Ti_3P structure was independently reported by Deardorff, Siemens, Romans & McCune (1969) in their study of the Nb–Si system. They supplied a single crystal to Waterstrat, Yvon, Flack & Parthé (1975) who undertook the single-crystal study that we consulted for our crystallographic projection of the Ti_3P structure of Nb_3Si.

Fig. 1(*a*) and (*b*) are standard (001) projections of Nb_3Si in the Ti_3P and Cr_3Si structure respectively. From these two projections we will show that only a few elementary shifts in the atomic positions are needed to transform the Ti_3P into the Cr_3Si structure, and diffusion is not a necessary condition for the structure transformation to occur. The lattice parameters for the tetragonal Ti_3P structure are $a_0 = 10{\cdot}224$ and $c_0 = 5{\cdot}189$ Å, $Z = 8$, and the lattice parameter for the cubic Cr_3Si structure is $a_0 = 5{\cdot}091$ Å, $Z = 2$. The Cr_3Si structure is subsequently 2·8% denser than the Ti_3P structure at ambient conditions. The two projections are scaled to relative cell dimensions, but this disagrees with dimension scaling by only 0·4% in the plane of the projection and 2% in the vertical dimension. Thus, the two projections can be considered as having the same scale for our comparison.

Despite the complex appearance of the Ti_3P structure, it is similar to the Cr_3Si structure. This is best shown by outlining the body-centered cells formed by the Si atoms in both structures. These are shown as solid lines in Fig. 1(*a*) and (*b*). The Si atoms in both structures occupy the same relative positions. By dividing the projections into three different types of cell stacks, labeled *A*, *B*, and *C* and outlined with dashed lines, we will see how the Ti_3P structure can transform to the Cr_3Si structure by only two simple shifts of the Nb atoms, followed by minor readjustments of the atoms' positions.

The most important Nb-atom repositioning in the Ti_3P structure to achieve the characteristics of the Cr_3Si structure occurs in cell stack *A*. For the relative arrangement of the Nb atoms in cell stack *A* in the Ti_3P structure to have a similar arrangement to those in cell stack *A* in the Cr_3Si structure, the column of Nb atoms must rotate 45° about an axis running down the center of the cell stack and glide along the axis about one quarter of a cell length, in this case, 1·25 Å.

The increased efficiency of packing due to this screw rotation of the Nb chain can be more easily seen in the packing drawing in Fig. 2. This is a drawing of cell *A* as viewed from a horizontal perspective as indicated in Fig. 1(*a*) and (*b*), labeled 1. The relative atom sizes are based on atomic radii in 12-fold coordination. As the Nb column or chain, made up of horizontal pairs of Nb atoms joined perpendicular to one another, rotates and glides about its common axis, each Nb atom moves from a position where it is in contact with two Si atoms

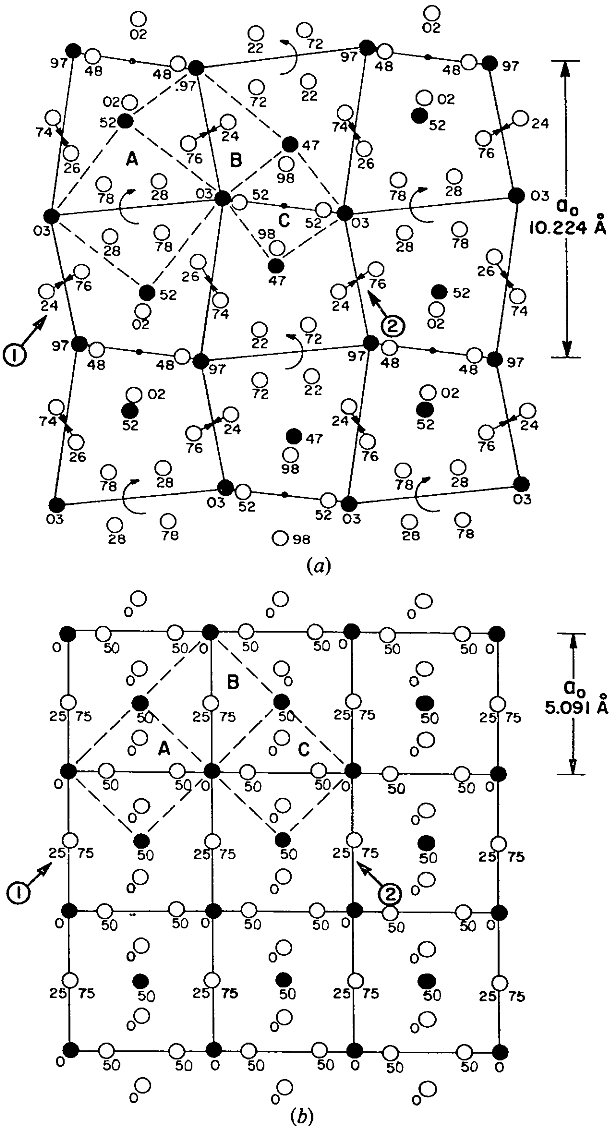

Fig. 1. The (001) projections of (*a*) the Ti_3P structure and (*b*) the Cr_3Si structure. The filled circles represent Si-atom sites and the open circles represent Nb-atom sites. The number beside each site circle indicates the height of the site in fractions of a cell length $\times 10^2$. The solid lines outline the body-centered Si-atom lattices throughout both structures. The structures are also divided into smaller cells labeled *A*, *B* and *C*. It is in these cells that three different atomic repositionings or shifts occur in order to transform from one structure to another as discussed in the text. The circled numbers refer to directions of inplane views drawn in Figs. 2 through 6.

(Ti_3P) to a position where it is in contact with four Si atoms (Cr_3Si). The Si atoms in the Ti_3P structure rest in the clefts of two Nb atoms, but in the Cr_3Si configuration, the Si atoms nest between four Nb atoms. The cell's volume is 94·7 Å^3 in the Ti_3P structure and 66 Å^3 in the Cr_3Si structure.

The direction in which the Nb atoms glide can be in the opposite direction, of course, in which case the rotation would also be in the opposite direction. But, given a direction of shift for the Nb chain in the type-*A* cell stacks, rotation directions at neighboring type *A* cells are opposite. The various type-*A* cell sites throughout the Ti_3 projection in Fig. 1(*a*) are shown as circular arrows, indicating the direction of rotation given a shift direction.

Once the Nb-atom columns complete the 45° rotation and quarter cell length glide at the *A*-cell stack sites, the structure is essentially that of the Cr_3Si or *A*15. The Si atoms are in the body-centered positions and the Nb atoms are formed into chains running perpendicular to each other throughout the lattice, the essential characteristics of the Cr_3Si structure.

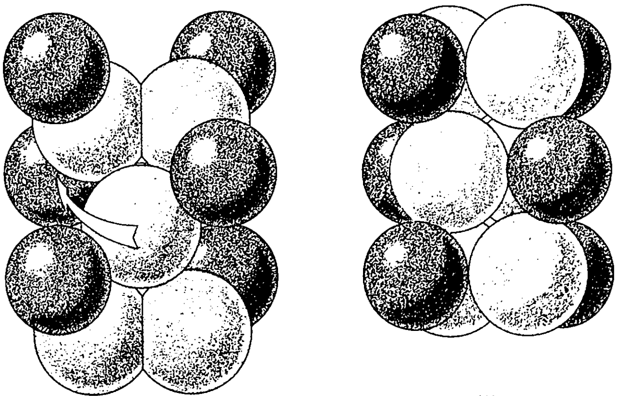
(*a*) (*b*)

Fig. 2. Packing model of cell *A*, view 1, in the (*a*) Ti_3P and (*b*) Cr_3Si structures. The light spheres represent Nb atoms and the dark spheres represent Si atoms. The arrow shows the repositioning of the Nb atom undergoing a screw rotation.

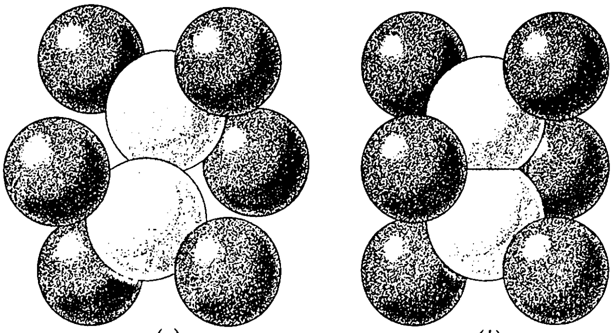
(*a*) (*b*)

Fig. 3. Packing model of cell *B*, view 1, in the (*a*) Ti_3P and (*b*) Cr_3Si structures. The light spheres represent Nb atoms and the dark spheres Si atoms.

The edge Si atoms of cell *A* can move toward the axis of the cell after the screw rotation as shown in Fig. 2. Thus, the edge of cell *A* is reduced in size from 4·2 to 3·6 Å. Likewise, the cell edges of cell *B* bordering the two neighboring *A*-type cells are contracted. If the Nb-atom positions in cell *B* of Fig. 1(*a*) and (*b*) are compared, they show that the Nb atoms of the Ti_3P structure have to shift 0·8 Å horizontally toward each

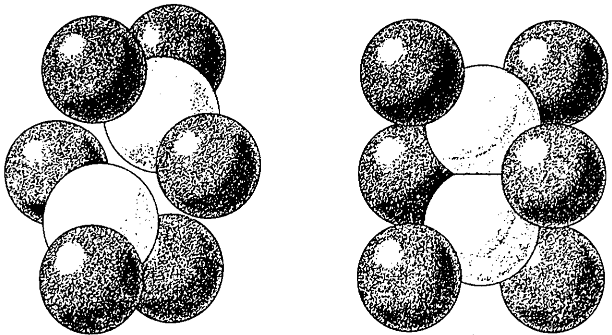
(*a*) (*b*)

Fig. 4. Packing model of cell *B*, view 2, in the (*a*) Ti_3P and (*b*) Cr_3Si structures. The light spheres represent Nb atoms and the dark spheres Si atoms.

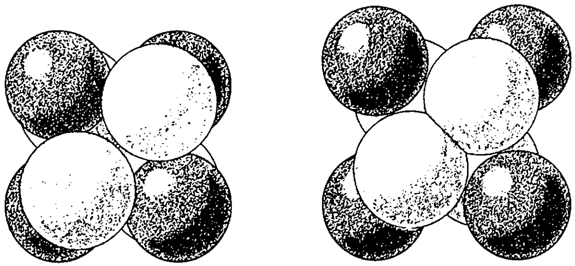
(*a*) (*b*)

Fig. 5. Packing model of cell *C*, a top view along projection (001) in the (*a*) Ti_3P and (*b*) Cr_3Si structures. This illustrates how the tight packing of this cell in the Ti_3P structure appears to force the Si atoms into the normally tightly bound Nb pair and force them apart. The light spheres represent Nb atoms and the dark spheres Si atoms.

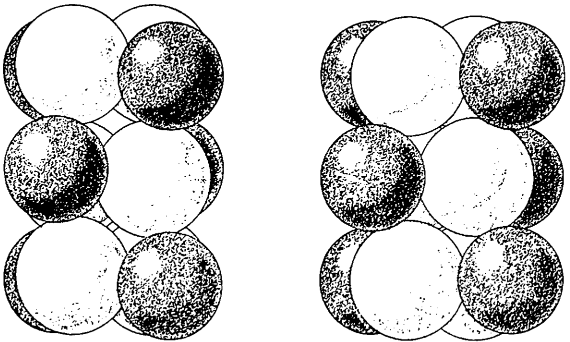
(*a*) (*b*)

Fig. 6. Packing model of cell *C*, view 2, in the (*a*) Ti_3P and (*b*) Cr_3Si structures. The light spheres represent Nb atoms and the dark spheres Si atoms.

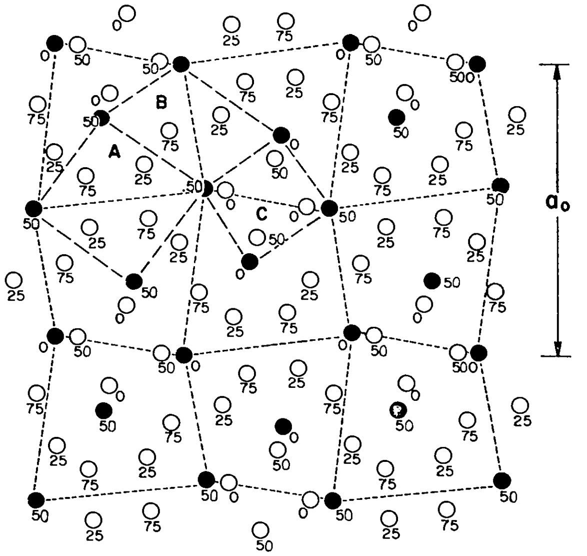

Fig. 7. The (001) projection of the Fe_3P structure presented in a comparable way to the projections in Fig. 1. The main point to be illustrated is that though this structure is similar to the Ti_3P structure, the body-centered lattice of the minor component does not exist.

other in order to be positioned along the same axis as the Nb atoms are in cell *B* of the Cr_3P structure. The *B*-cell-edge contraction may initiate the movement of the Nb atoms into this linear array. Figs. 3 and 4 show packing drawings of the *B* cell from a horizontal perspective from two different viewpoints, views 1 and 2, shown in Fig. 1(*a*) and (*b*). The sites at which this contraction of Nb atoms into a single column occurs in the Ti_3P structure are shown as the sets of contracting arrows in the projections in Fig. 1(*a*). As can be seen, the directions of contraction at neighboring sites are perpendicular to each other. In going from the Ti_3P to the Cr_3Si structure this cell's volume increases slightly, from 64·8 $Å^3$ to 66 $Å^3$.

The remaining cell type is *C*. The atomic arrangements in the *C*-cell stack in the Ti_3P and the Cr_3Si structures are nearly the same. The packing in this cell in the Ti_3P structure is much denser than in the Cr_3Si structure, so much so that in a hard-sphere interpretation, the Si atoms on the edges of this tetragonal cell are forced toward the axis of the cell forcing apart the Nb pairs. In the Cr_3Si structure, the packing density in the cell is less and the Nb atoms are tightly paired. Packed drawings of this cell in the two structures in the plane of the projection are compared in Fig. 5(*a*) and (*b*). Horizontal views of this cell are compared in Fig. 6(*a*) and (*b*). The volume of the *C* cell in the Ti_3P structure is 46·8 $Å^3$ and in the Cr_3Si structure, 66 $Å^3$.

In Fig. 7 is displayed the Fe_3P structure, which is very similar to the Ti_3P structure. We have outlined with small-dash lines the same cells that were outlined with solid lines in Fig. 1, where the Si atoms were arranged in a body-centered configuration. In the Fe_3P structure, however, the minor component is no longer in a body-centered configuration, and to rearrange the atoms into the Cr_3Si structure would appear to require some extensive atom shifts. Ta_3Si can be quenched or annealed into either the Ti_3P or the Fe_3P structure. It would be of interest to recover both phases of this compound from shock compression and from static high pressures and temperatures to see if either phase had transformed to the Cr_3Si structure.

Conclusion

The Ti_3P structure of Nb_3Si has been shock compressed and on recovery has been found to have transformed to the Cr_3Si structure. From an examination of both the Ti_3P and Cr_3Si structures, it was found that the former could be transformed to the latter by a screw rotation of a column of Nb-atom pairs with slight repositioning of the remainder of the structure. This accounts for the rapidity of the transformation under shock compression. The Fe_3P structure cannot be so easily transformed to the Cr_3Si structure based on inspection of the two structures.

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