

# The kinetics of pressure-induced fcc-bcc transformation in ytterbium

C. Divakar, Murali Mohan, and A. K. Singh

Materials Science Division, National Aeronautical Laboratory, Bangalore 560 017, India

(Received 10 November 1983; accepted for publication 12 March 1984)

The kinetics data for the pressure-induced fcc→bcc transformation in ytterbium under isobaric-isothermal conditions in the pressure range 3.3–4.6 GPa have been reported. The kinetics data satisfy Avrami equation:  $\xi = 1 - \exp[-(t/\tau)^n]$ , where  $r$  and  $n$  are constants at a given pressure. Both  $r$  and  $n$  decrease with increase in pressure, as given by the following relations:

$\ln r = (36.2 \pm 1) - (6.8 \pm 0.3)p$ , and  $n = 1.36 + 0.55p - 0.168p^2$ , where  $p$  is pressure (GPa). The activation free energy for the combined process of nucleation and growth has been estimated from the  $r-p$  data and is found to decrease with increase in pressure. The activation free energy varies from 16 kcal mol<sup>-1</sup> at 3.3 GPa to 11 kcal mol<sup>-1</sup> at 4.6 GPa. The activation enthalpies at 3.3, 3.6, and 3.8 GPa have been determined by measuring  $\tau$  at different temperatures. The activation volume is  $-17 \text{ cm}^3 \text{ mol}^{-1}$  at 300 K. It is estimated from the  $r-p$  data that fcc-bcc transformation under shock loading will occur at about 7 GPa.

## I. INTRODUCTION

Ytterbium in the fcc phase, which is stable at one atmosphere and room temperature, is a semimetal,<sup>1</sup> and transforms to a semiconducting state<sup>1-3</sup> at nearly 1.4 GPa. The semiconducting fcc phase transforms to bcc phase at 4 GPa.<sup>4</sup> The fcc-bcc transformation is reported to be sluggish and is accompanied by a large decrease in electrical resistance.<sup>2,5</sup> The volume change at the transformation is about 3%.<sup>4</sup> We find that the fcc-bcc transformation is time dependent and occurs over a wide range of pressures. In this paper we report the results of the measurements, under isobaric-isothermal condition, of the fcc-bcc transformation in ytterbium at  $300 \pm 3 \text{ K}$  in the pressure range 3.3–4.6 GPa. The various parameters (activation energy, activation volume and the characteristic time) have been obtained.

## II. EXPERIMENT

A tungsten carbide opposed anvil setup (anvil face: 12.7 mm diameter) with pyrophyllite gasket was used to pressurize the specimen. The experiments were mostly done with talc as the pressure transmitting medium. A few experiments were also done using cast epoxy as the pressure transmitting medium. The relation between applied load  $L$  and the specimen pressure  $p$  was determined using the well-known transitions in bismuth and thallium. These experiments indicated that the  $L-p$  relation was very nearly linear in the region 2.5–7.6 GPa. For a given pair of anvils, the  $L-p$  relation mainly depends on the gasket thickness. A careful control over the dimensions of the gasket and pressure transmitting talc discs in each run gave a highly reproducible  $L-p$  relation. The uncertainty in the specimen pressure was reduced further by placing in each run a bismuth specimen at right angles to the ytterbium specimen, the two being insulated by a thin piece of mica. The resistance of the ytterbium specimen was measured using a four-lead arrangement. The bismuth transitions were detected using a two-lead setup. The details of the pressure cell and lead arrangement are given in an earlier paper.<sup>6</sup>

The specimen was pressurized at a rate  $0.1 \text{ GPa min}^{-1}$  up to 2.54 GPa as indicated by the first bismuth transition. The desired pressure in the range 3.3 to 4.6 was reached by rapid pressurization ( $0.06 \text{ GPa s}^{-1}$ ). The pressure in the range 3.3–4.6 GPa were also reached with the help of a step-loading arrangement.<sup>7</sup> With the help of a constant-current source the current in the ytterbium specimen was maintained constant. The output of the voltage leads, which was proportional to the specimen resistance, was fed to a strip chart recorder. As the transformation progressed with time, the specimen resistance dropped. The transformation was considered complete when the specimen resistance did not change with time. The completion of the transformation was further confirmed by slightly increasing the pressure which led to only a small decrease in resistance; the calculated pressure coefficient of resistance was typical of the bcc phase. The fraction  $\xi$  of the bcc phase as a function of time was calculated from the resistance-time data by the method discussed earlier.<sup>6</sup>

The resistance-time data were also obtained above room temperature. For these measurements the following sequence of steps was employed. The pressure was increased at a rate  $0.1 \text{ GPa min}^{-1}$  up to first Bi transition, and held constant. The anvils were then heated to the desired temperature. The pressure was increased to the desired value by step-loading. After the completion of the transformation, the anvils were allowed to cool to room temperature. The pressure was then increased to the second Bi transition. The loads at which the two Bi transitions occurred were used to determine the pressure of the experiment.

## III. RESULTS AND DISCUSSION

### A. Incubation time

The transformation is preceded by an incubation time  $t_i$ . This is the time interval between the application of final pressure and the start of the transformation. The sensitivity of the recording system in the present experiments permitted

detection of as low as 0.05% transformation. The incubation time, therefore, is sum of true incubation time and the time for 0.05% transformation. The zero time for the  $\xi-t$  data was taken at the start of the transformation. A plot of  $t_i$  versus pressure is shown in Fig. 1. It is seen that  $t_i$  decreases rapidly with increase in pressure;  $t_i$  is nearly 30 h at 3.3 GPa and drops to about 55 s at 4.0 GPa. A straight line fitted to the  $\ln t_i - p$  data by the method of least squares gives the following result:

$$\ln t_i = 47.6 (\pm 2) - 10.9 (\pm 0.5)p. \quad (1)$$

## B. Kinetics data

The equations describing the kinetics of transformations involving nucleation and growth were discussed extensively by Avrami,<sup>8-10</sup> and Johnson and Mehl.<sup>11</sup> Alternative methods of deriving these equations have been given by several authors, for example, Christian.<sup>12</sup> One begins with a general model wherein critically sized nuclei of the new phase are formed at a rate  $I$ . Such nuclei grow with a velocity  $u$ . Considering the impingement of regions growing from different nuclei, the volume fraction  $\xi$  of the new phase at a time  $t$  is given by

$$-\ln(1 - \xi) = \frac{4\pi}{3} u^3 \int_0^t I(t - t')^k dt', \quad (2)$$

where  $k$  refers to the dimensionality of growth. For a three-, two-, and one-dimensional growth,  $k$  is respectively 3, 2, and 1. If the time dependence of  $I$  is known, the integral in Eq. (2) can be evaluated. For a constant nucleation rate Eq. (2) can be simplified as follows:

$$\xi = 1 - \exp\left(-\left(\frac{t}{\tau}\right)^n\right), \quad (3)$$

where  $n$  and  $T$  are constants. Further, for homogeneous nucleation decreasing with time,  $3 < n < 4$ ,  $2 < n < 3$ , and  $1 < n < 2$  for a three-, two-, and one-dimensional growth. In

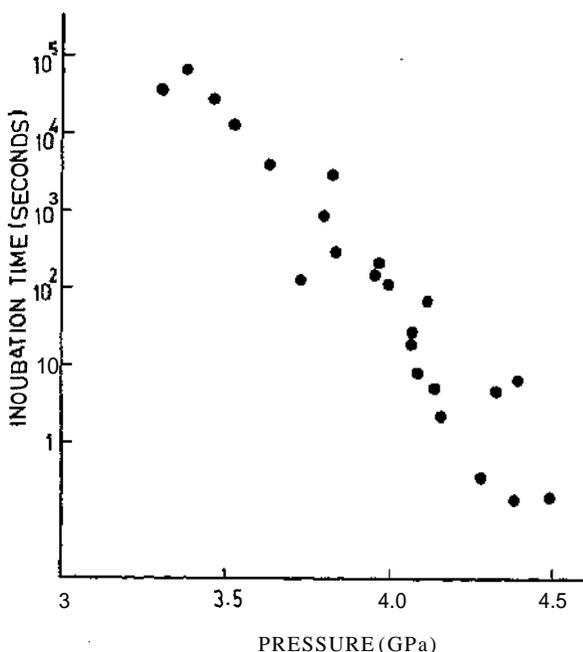


FIG. 1. The pressure dependence of incubation time at 300 K.

polymorphic transformation,  $n = 1$  can occur if grain boundary nucleation after site saturation takes place.<sup>12</sup>

The present  $\xi - t$  data satisfy Eq. (3) in the entire pressure range. (The zero of time scale has been taken at 0.05% transformation). The parameters  $n$  and  $r$  are found to be pressure dependent. A polynomial fitted to the  $n-p$  data, shown in Fig. 2 yields the following result

$$n = 1.36 + 0.55p - 0.168p^2. \quad (4)$$

These data indicate that  $n < 1$  above 3.8 GPa. The brief discussion of Eq. (3) given above suggests that the lowest value of  $n$  is 1. The actual situations which could lead to  $n < 1$  are being examined.

The variation of  $r$  with pressure is shown in Fig. 3. It is seen that  $T$  decreases rapidly with increase in pressure. On fitting to the  $\ln r - p$  data a straight line by the method of least squares the following result is obtained:

$$\ln r = (36.2 \pm 1) - (6.8 \pm 0.2)p. \quad (5)$$

## C. Energetics of transformation

In terms of activation free energy,  $r$  is given by the following relation:

$$\ln r = b_0 + \Delta\bar{G}/RT, \quad (6)$$

where  $b_0$  is a constant,  $A\bar{G}$  is the activation free energy for the combined process of nucleation and growth, and  $R$  is gas constant. It is seen experimentally [Eq. (5)] that  $r$  depends on pressure. In Eq. (6) the pressure dependence of  $r$  can arise because either  $b_0$  or  $A\bar{G}$  (or both  $b_0$  and  $A\bar{G}$ ) is pressure dependent. In the following discussions it is assumed that  $A\bar{G}$  decreases with increase in pressure and  $b_0$  is independent of pressure. These assumptions are supported by the temperature experiments discussed later in this paper. On combining Eqs. (5) and (6) the following result is obtained:

$$\Delta\bar{G}/RT = 36.2 - b_0 - 6.8p. \quad (7)$$

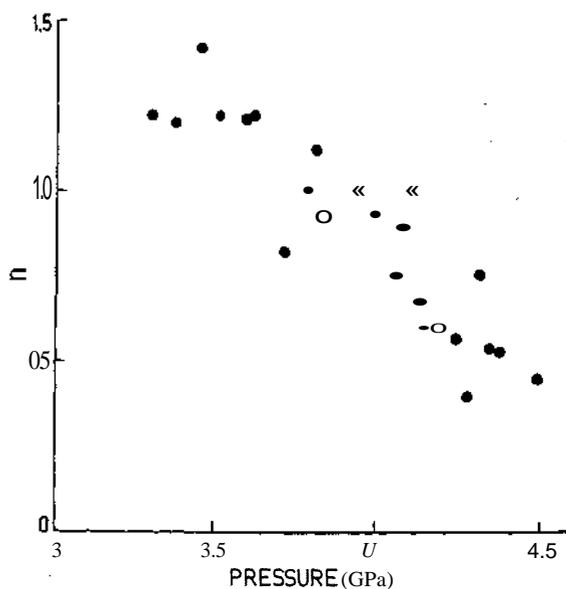


FIG. 2. The pressure dependence of  $n$  at 300 K.

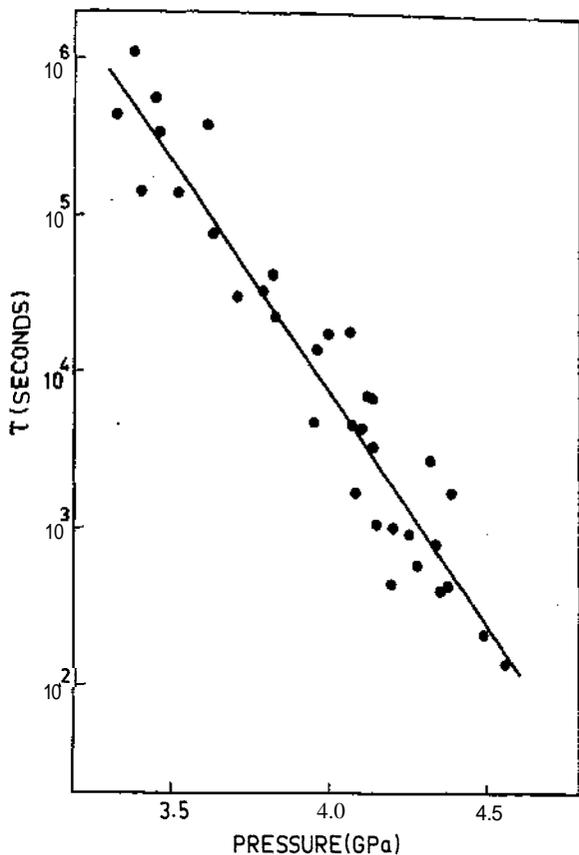


FIG. 3. The pressure dependence of  $\tau$  at 300 K.

The values of  $A\bar{G}$  at various pressures can be calculated if  $b_0$  is known. A rough estimate of  $b_0$  can be made from the following considerations. It is seen from Eq. (6) that, for a given  $b_0$ ,  $\ln r$  decreases with decreasing  $A\bar{G}$ . The smallest value of  $T$  occurs when  $A\bar{G} = 0$ . In absence of any barrier, the speed of transformation will be controlled by the response of a solid to the disturbances caused by the transformation. The speed with which these disturbances can propagate will be limited by the relaxation time of the lattice. The disturbances and therefore the transformation will proceed with velocity of sound in the solid. Since the velocity of sound in solids is typically a few  $\text{km s}^{-1}$ ,  $\tau$  under these conditions is of the order of  $10^{-6}$  s. With  $\Delta\bar{G} = 0$  and  $r = 10^{-6}$  s in Eq. (6),  $b_0 = -13.8$  is obtained.

It is seen from Eq. (6) that  $r = 10^{-6}$  s can occur if

$$b_0 + \Delta\bar{G}/RT = -13.8. \quad (8)$$

Thus, any combination of  $b_0$  and  $A\bar{G}$  values which satisfy Eq. (8) will lead to  $\tau = 10^{-6}$  s. The case  $b_0 = -13.8$  represents the largest value of  $b_0$ , which occurs at  $A\bar{G} = 0$ , for which  $r = 10^{-6}$  s is possible. For  $b_0 < -13.8$ ,  $r = 10^{-6}$  s can occur at some positive nonzero value of  $\Delta\bar{G}$ . The case  $b_0 = -13.8$  has been used in estimating  $\Delta\bar{G}$  because it leads to reasonable agreement with the results of the temperature experiments described later in this paper. The variation of  $A\bar{G}$  with pressure as obtained from Eq. (7) with  $b_0 = -13.8$  is shown in Fig. 4.

#### D. Transformation under shock loading

The fcc  $\rightarrow$  bcc transformation is likely to occur also under shock loading at a pressure at which  $r = 10^{-6}$  s, because

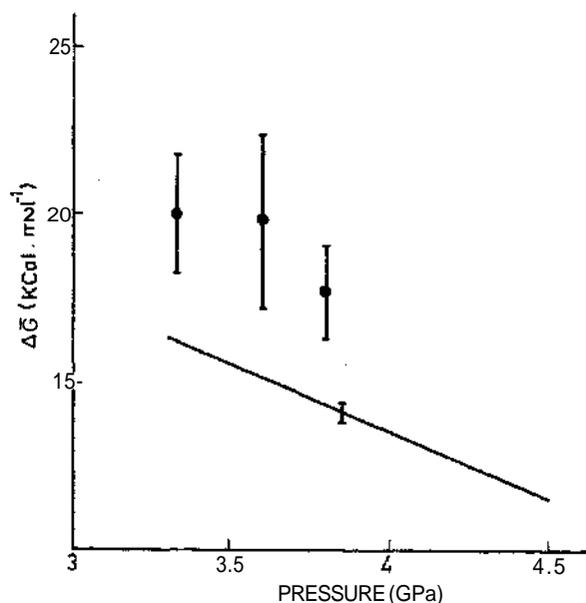


FIG. 4.  $\Delta\bar{G}$  as a function of pressure as obtained from Eq. (7) with  $b_0 = -13.8$ . The dots indicate the values of activation enthalpies determined from  $\ln r$  vs  $1/T$  plot.

then the kinetics of transformation becomes fast enough for the system to respond to shock pressure pulse with a typical time duration of a few microseconds. From Eq. (5) it is seen that  $r = 10^{-6}$  s at  $p = 7.4$  GPa. Thus, neglecting the temperature effects during shock loading one would expect ytterbium to undergo fcc  $\rightarrow$  bcc transformation at 7.4 GPa under shock loading. However, the transformation under shock loading may occur much below 7.4 GPa if the temperature rise on shock loading is appreciable, because the kinetics of transformation becomes faster at higher temperatures (present study, Sec. III E j), and also the transformation pressure decreases with increase in temperature.<sup>5</sup>

Ytterbium under shock loads has been studied by Gust and Royce<sup>13</sup> and Carter *et al.*<sup>14</sup> In both these studies the particle velocity versus shock velocity curve showed a break in slope at nearly 15 GPa, indicating a phase transformation. This phase transformation has been identified as melting<sup>13,14</sup> and not a structural transformation. Further, the Hugoniot temperature at 7.4 GPa estimated from these data is about 600 K. Such a rise in specimen temperature will enhance the kinetics, and the transformation under shock loading is likely to occur at pressures significantly below 7.4 GPa. The shock wave data of Carter *et al.*<sup>14</sup> do not indicate the occurrence of the fcc  $\rightarrow$  bcc transformation. The results of Gust and Royce<sup>13</sup> contain only one datum point below 7 GPa. The experimental set up used in both these studies are designed for high pressures ( $> 10$  GPa). It would be interesting to conduct the experiments on ytterbium using a shock wave set up suitable for low pressure range.<sup>15</sup>

#### E. Activation enthalpy

In terms of the activation entropy  $\Delta\bar{S}$  and the activation enthalpy  $\Delta\bar{H}$ , Eq. (6) can be rewritten as

$$\ln \tau = b_0 - (\Delta\bar{S}/R) + (\Delta\bar{H}/RT). \quad (9)$$

This equation suggests that  $\Delta\bar{H}$  can be determined if  $\tau$  is

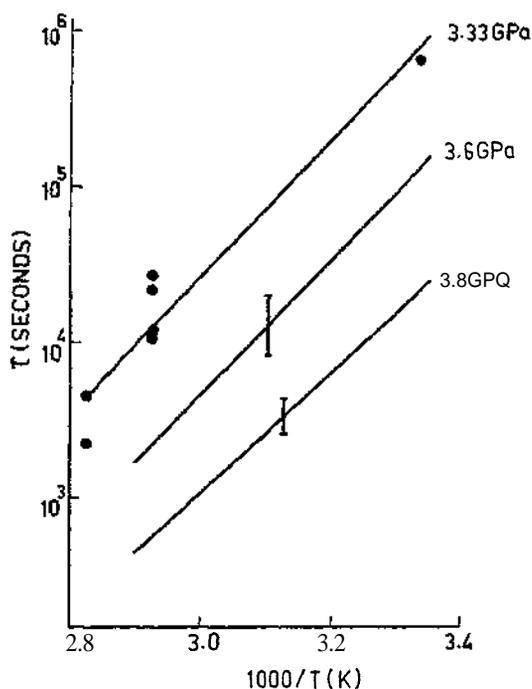


FIG. 5.  $\ln TV S1/Tp$  plot.

measured at different temperatures. At 3.3 GPa experiments were carried out at 300, 340, and 355 K and  $r$  values determined. The  $A\bar{H}$  value could be obtained from the  $\ln r$  vs  $1/T$  plot. The experiments were also done at 3.6 and 3.8 GPa, but at these pressures the highest temperature was 340 K. The  $\ln T$  vs  $1/T$  plot is shown in Fig. 5. The  $A\bar{H}$  values thus obtained are marked by solid dots in Fig. 4. The rather small range over which the temperatures could be varied, leads to relatively large error in the  $A\bar{H}$  values. The activation entropy was estimated from the experimentally obtained intercept of the  $\ln r$  vs  $1/T$  plot using  $b_0 = -13.8$ . Over the pressure range 3.3–3.8 GPa, activation entropy was constant within the experimental error, and the average value was  $13 \pm 2 \text{ cal mol}^{-1} \text{ K}^{-1}$ .

It would be desirable to do these experiments over a wider range of temperatures. However, the following considerations limit the highest temperatures at which these experiments can be conducted. As has been discussed in Sec. II, the specimen is initially pressurized to 2.54 GPa (pressure of Bi I–Bi II transition) and heated to the desired temperature. The specimen pressure is then raised to the desired value by step loading. If the temperature is high, then the transformation starts during the heating period. This happens partly because the kinetics of the transformation becomes faster at higher temperature, and partly because the specimen pressure slightly increases on heating. For these reasons the temperature above 355 K could not be reached in the experiments at 3.3 GPa. At 3.6 and 3.8 GPa, the kinetics of transformation above 340 K became so fast that appreciable transformation took place before the desired pressure could be reached.

### F. Activation volume

It can be easily shown that the activation volume  $V^*$  is given by

$$V^* = \left( \frac{\partial \ln \tau}{\partial p} \right)_T RT. \quad (10)$$

The present  $\ln \tau$  vs  $p$  data (Fig. 3) give  $V^* = -17(\pm 1) \text{ cm}^3 \text{ mol}^{-1}$ . It is possible to obtain  $F^*$  values for any fraction  $\xi$  by simply replacing  $r$  by  $t_\xi$ , the time for a given fraction of transformation  $\xi$ . It is found that  $V^*$  is dependent on  $\xi$ . The value of  $F^*$  is  $-22(\pm 1)$  and  $-15(\pm 1) \text{ cm}^3 \text{ mol}^{-1}$  for respectively  $\xi = 0.1$  and 0.9. A similar behavior was observed by Hall and Merrill<sup>16</sup> who reported  $F^* = -30 \text{ cm}^3 \text{ mol}^{-1}$  for  $\xi = 0.1$  and  $F^* = -17 \text{ cm}^3 \text{ mol}^{-1}$  for  $\xi = 0.98$ .

### G. Equilibrium pressure

The thermodynamic equilibrium pressure for fcc-bcc transformation has not been determined. However, it has been suggested that it is close to 4 GPa.<sup>3</sup> This suggestion is based on the fact that the ytterbium is found to transform at 4.0 GPa in the experiments wherein pressure is increased continuously or in steps with reasonable waiting time (a few minutes). In the present experiments, the transformation is found to occur even at 3.3 GPa. Since a transformation can occur only if the applied pressure is more than the equilibrium pressure, the present data suggest that equilibrium pressure is well below 3.3 GPa.

### IV. CONCLUSIONS

- (1) The kinetics data fit Avrami equation in the range 3.3–4.6 GPa; this indicates that the fcc-bcc transformation in ytterbium involves the processes of nucleation and growth.
- (2) The activation free energy for the combined process decreases with the increase in pressure. The activation free energy is  $16 \text{ kcal mol}^{-1}$  at 3.3 GPa and decreases to  $11 \text{ kcal mol}^{-1}$  at 4.6 GPa.
- (3) The transformation under shock loading is likely to occur below 7.4 GPa.
- (4) The thermodynamic equilibrium pressure is below 3.3 GPa.

<sup>1</sup>D. B. McWhan, T. M. Rice, and P. H. Schmidt, *Phys. Rev.* **177**, 1063 (1969).

<sup>2</sup>R. A. Stager and H. G. Drickamer, *Science* **139**, 1284 (1963).

<sup>3</sup>P. C. Souers and G. Jura, *Science* **140**, 481 (1963).

<sup>4</sup>H. T. Hall, J. D. Barnett, and L. Merrill, *Science* **139**, 111 (1963).

<sup>5</sup>A. Jayaraman, *Phys. Rev.* **135**, A1056 (1964).

<sup>6</sup>A. K. Singh, Murali Mohan, and C. Divakar, *J. Appl. Phys.* **54**, 5721 (1983).

<sup>7</sup>A. K. Singh, C. Divakar, and Murali Mohan, *Rev. Sci. Instrum.* **54**, 1407 (1983).

<sup>8</sup>M. Avrami, *J. Chem. Phys.* **7**, 1103 (1939).

<sup>9</sup>M. Avrami, *J. Chem. Phys.* **8**, 212 (1940).

<sup>10</sup>M. Avrami, *J. Chem. Phys.* **9**, 177 (1941).

<sup>11</sup>W. A. Johnson and R. F. Mehl, *Trans. Am. Inst. Min. Metall. Pet. Eng.* **135**, 416 (1939).

<sup>12</sup>J. W. Christian, *The Theory of Transformations in Metals and Alloys, Part I. Equilibrium and General Kinetic Theory* (Pergamon, New York, 1975), pp. 19, 542.

<sup>13</sup>W. H. Gust and E. B. Royce, *Phys. Rev. B* **8**, 3595 (1973).

<sup>14</sup>W. J. Carter, J. N. Fritz, S. P. Marsh, and R. G. McQueen, *J. Phys. Chem. Solids* **36**, 741 (1975).

<sup>15</sup>Z. Rosenberg, *J. Appl. Phys.* **53**, 1474 (1982).

<sup>16</sup>H. T. Hall and L. Merrill, *Inorg. Chem.* **2**, 618 (1963).