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EFFECT OF TEMPERATURE ON THE ELECTRONIC INSTABILITY AND THE CRYSTALLINE PHASE CHANGE AT LOW TEMPERATURE OF V_3Si TYPE COMPOUNDS

J. Labbé and J. Friedel

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16. Abstract
Equations assuming a Jahn-Teller-type effect for the d band electrons in V_3Si compounds are given, and the results of free-energy change calculations by using some approximations based on these equations are depicted. The tetragonal structure is converted to cubic as the temperature rises past T_m, which is calculated as 13°K., by the Batterman-Barrett method and is measured to be 20-5°K. Other parameters such as change of C_p with temperature are predicted better.

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EFFECT OF TEMPERATURE ON THE ELECTRONIC INSTABILITY AND THE CRYSTALLINE PHASE CHANGE AT LOW TEMPERATURE OF V_3Si TYPE COMPOUNDS

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Introduction

In a preceding article [6], we showed that a Jahn-Teller effect on the d band structure can explain the instability of the cubic phase of type V_3Si intermetallic superconductor compounds at zero temperature, with the tetragonal phase being stable. In this second part, we study the effect of temperature. By applying Fermi statistics to our model, we show that the cubic phase recovers its stability above a certain temperature. This allows the martensite transition observed at low temperature by Batterman and Barrett [4] to be understood. In addition, we show that, in our model, the transition very likely is of the first order but, meanwhile, it is only accompanied by slight discontinuities in the variation of different physical parameters, such as lattice distortion and the elastic constants. Likewise, the latent heat of transformation certainly is very low. /303

In the second section, we stress more particularly the variation of the elastic constants with temperature, and we show that the experimental results obtained by Testardi, Bateman, Reed and Chirba [3] really appear to reveal a first order transition.

In the third section, we apply our calculations numerically to the example of V_3Si.

1. Effect of temperature and order of the transition

For a finite value of the temperature T, we have to find the value of ε which gives the minimum free energy F=U-TS. The Fermi level E'_F is a function of ε and T. Its value is given by the equation

$$\int_{E_{m1}}^{-E_{m1}} \frac{n_1(E)\,dE}{1+\exp\frac{E-E'_F}{kT}} + 2\int_{E_{m2}}^{-E_{m2}} \frac{n_2(E)\,dE}{1+\exp\frac{E-E'_F}{kT}} = 3\int_{E_m}^{E_F^{(0)}} n(E)\,dE = 3Q \qquad \text{(II.1)}$$

where $E_F(0)$ is the Fermi level for $\varepsilon=0$ and $T=0$. At a nonzero temperature, no band is ever completely empty and we cannot distinguish the cases $\varepsilon<\varepsilon_c^-$, $\varepsilon_c^-<\varepsilon<\varepsilon_c^+$ and $\varepsilon_c^+<\varepsilon$.

The free energy is a function of ε and T; for a given temperature T, its variation with ε is written:

$$\begin{aligned} dF = -kT \Big\{ & N \int_{E_{m1}}^{-E_{m1}} n_1(E) \operatorname{Log}\left(1+\exp\frac{E'_F-E}{kT}\right) dE \\ & + 2N \int_{E_{m2}}^{-E_{m2}} n_2(E) \operatorname{Log}\left(1+\exp\frac{E'_F-E}{kT}\right) dE \\ & - 3N \int_{E_m}^{-E_m} n(E) \operatorname{Log}\left(1+\exp\frac{E_F-E}{kT}\right) dE \Big\} + 3NQ(E'_F-E_F) + 3N\frac{1}{2}A'\varepsilon^2 \end{aligned} \quad \text{(II.2)}$$

where E_F is the Fermi level at temperature T and $\varepsilon=0$, and recalling that there are $3N$ transition atoms in all in the crystal and Q electrons per transition atom in the d band under consideration. In (II.2), the variation of the contributions to entropy with ε, other than that of the d electrons, is disregarded. /304

Equation (II.1) can be solved numerically by machine calculation. By successive approximations, E'_F is calculated for various values of ε and T. The corresponding numerical values of dF are then obtained from (II.2). In this way, a system of curves is obtained, which respresents variations of dF with ε for various temperatures. Fig. 1 shows the system obtained in this way for V_3Si, as we shall see in Section 3. It is seen that the cubic phase ($\varepsilon=0$) again becomes stable above a certain temperature T_m.

In conclusion, at very low temperatures, the electrons remain confined in the bottom of the band, where the density of states is very high, which involves instability of the cubic phase. On the other hand, when the temperature rises, the band filling is modified, to the benefit of a lower density of states, which reduces the effect of electron instability. The presence of the term $1/2\, A'\varepsilon^2$, which changes very little with temperature, thus permits the cubic phase to regain its stability. To determine the order of the transition, we have to find the detailed shape of the curves which correspond to neighboring temperatures of T_m, for very small deformations ε. Then, dF can be expanded with respect to ε, and the order of the transition can be found, in such a way that the coefficients of this expansion vary with temperature. Therefore, if the following is written:

$$dF = 3N\left\{\frac{1}{2}A\varepsilon^2 + \frac{1}{3}B\varepsilon^3 + \frac{1}{4}C\varepsilon^4\right\} \quad \text{(II.3)}$$

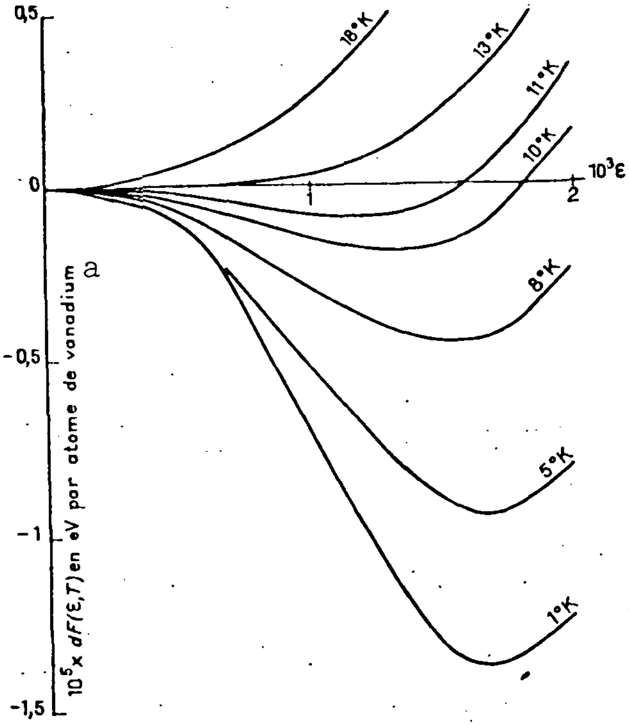

Fig. 1. Variations dF of free energy with distortion ε for various temperatures T.

Key: a. In eV per vanadium atom

coefficients A, B and C, obtained from (II.1) and (II.2) by calculations too long to be reproduced here, are expressed by:

$$A = \frac{1}{2} a^2 q^2 \int_{E_m}^{-E_m} E n(E) f(E)\,\mathrm{d}E + \frac{1}{2} a^2 q^2 \int_{E_m}^{-E_m} E^2 n(E) f'(E)\,\mathrm{d}E + A' \qquad \text{(II.4)}$$

$$B = -\frac{1}{8} a^3 q^3 \int_{E_m}^{-E_m} E n(E) f(E)\,\mathrm{d}E - \frac{3}{8} a^3 q^3 \int_{E_m}^{-E_m} E^2 n(E) f'(E)\,\mathrm{d}E - \frac{1}{8} a^3 q^3 \int_{E_m}^{-E_m} E^3 n(E) f''(E)\,\mathrm{d}E + B' \qquad \text{(II.5)}$$

$$C = \frac{11}{16} a^4 q^4 \int_{E_m}^{-E_m} E n(E) f(E)\,\mathrm{d}E + \frac{7}{16} a^4 q^4 \int_{E_m}^{-E_m} E^2 n(E) f'(E)\,\mathrm{d}E - 2\chi^2 \int_{E_m}^{-E_m} n(E) f'(E)\,\mathrm{d}E + \frac{3}{8} a^4 q^4 \int_{E_m}^{-E_m} E^3 n(E) f''(E)\,\mathrm{d}E + \frac{1}{16} a^4 q^4 \int_{E_m}^{-E_m} E^4 n(E) f'''(E)\,\mathrm{d}E + C' \qquad \text{(II.6)}$$

f(E) is the Fermi function $1\Big/\left[1 + \exp\dfrac{E - E_F}{kT}\right]$ and f'(E), f"(E), f"'(E),...are its successive derivatives with respect to energy E. χ is the coefficient of the term in ε^2 in the expansion of displacement $E'_F - E_F$ of the Fermi level, and it is given by

$$\chi = \left\{ \frac{1}{4} a^2 q^2 \int_{E_m}^{-E_m} E n(E) f'(E)\,\mathrm{d}E + \frac{1}{4} a^2 q^2 \int_{E_m}^{-E_m} E^2 n(E) f''(E)\,\mathrm{d}E \right\} \Big/ \int_{E_m}^{-E_m} n(E) f'(E)\,\mathrm{d}E$$

B' and C' are the anharmonic contributions of the conduction elec- /305
trons and nontransition atoms; B' can be roughly estimated from the equation of state of Grüneisen. He finds $B' \simeq -6A'$ ($B' < 0$). It is very difficult to evaluate C', but we shall see that it is reasonable to disregard it in a certain temperature region.

A machine calculation permits A, B and C to be determined for various temperatures T. Figs. 2A, 2B and 2C also indicate the behavior of their variations with T, for the particular case of V_3Si.

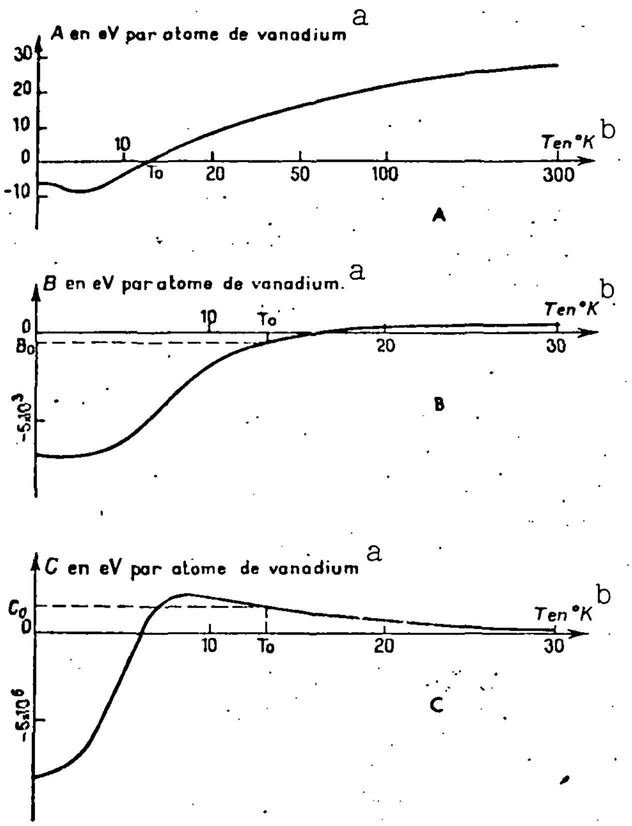

Fig. 2. Variations with temperature T of coefficients A, B and C of the expansion

$$dF = \frac{1}{2} A\varepsilon^2 + \frac{1}{3} B\varepsilon^3 + \frac{1}{4} C\varepsilon^4$$

of the free energy for very small distortions.

Key: a. In eV per vanadium atom
b. T in °K

It follows from the theory of Landau [1] that the transition can only be second order, if coefficients A and B cancel for the same temperature. In principle, this can occur for a well determined value of the initial filling of the band. But, this possibility can only be considered accidental. It would be quite extraordinary for the filling to have just the required value. On the other hand, group theory [2] shows that B has no cause to be identically zero due to crystal symmetry. Therefore, if the change in the structure under study here does not make any other parameter than uniform distortion ε interfere, the transition is certainly of the first order. But, we find that, in fact, in the cases of interest to us, coefficients A and B cancel for similar temperatures, so that, if the transition really is of the first order, it is, meanwhile, only accompanied by slight discontinuities in variation of the physical parameters. In addition, it only brings a low latent heat into play.

We call T_0 the temperature for which A cancels by changing sign. Generally, B and C are zero for this temperature, and the transition is first order. In the immediate vicinity of T_0, A can be expanded in $T-T_0$, and $A \simeq K(T-T_0)$ can be written, where K is a positive constant. If this vicinity is small enough, B and C can be identical to their values at T_0, or $B_0=B(T_0)$ and $C_0=C(T_0)$.

C_0 has to be positive for there to be a transition. The number of solutions of the equation $dF(\varepsilon)=0$ depends on the sign of the discriminant

$$\Delta = \frac{1}{9} B_0^2 - \frac{1}{2} C_0 K(T - T_0)$$

which cancels out for the temperature

$$T_m = T_0 + (2/9)(B_0^2/C_0 K) \qquad \text{(II.7)}$$

and there then is a double root

$$\varepsilon(T_m) = -(2/3)(B_0/C_0). \qquad \text{(II.8)}$$

The first order transition occurs at temperature T_m. B_0 can be positive or negative, according to the initial filling of the bands. Figs. 3A and 3B show the behavior of the variations of dF with ε for very close temperatures T_m, respectively, in the cases /306
$B_0>0$ and $B_0<0$.

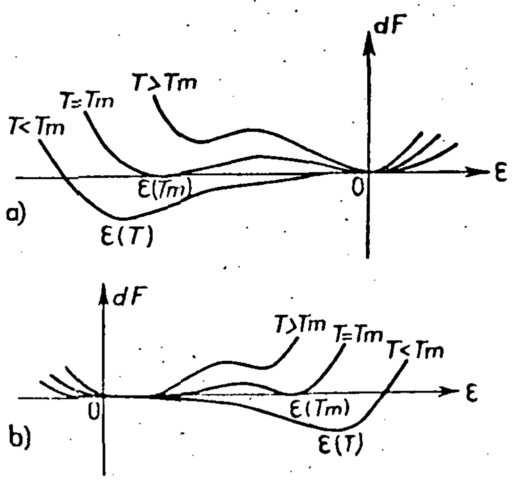

Fig. 3. Variations dF of free energy with distortion ε for temperatures T very near transition temperature T_m, in the cases $B_0>0$ (Fig. 3a) and $B_0<0$ (Fig. 3b).

The latent heat of transformation is equal to the variation ΔU of the internal energy between the states $\{T=T_m,\ \varepsilon=0\}$ and $\{T=T_m,\ \varepsilon=\varepsilon(T_m)\}$. The Helmoltz relation permits the writing of

$$\Delta U = \Delta F - T(\partial/\partial T)(\Delta F). \qquad \text{(II.9)}$$

The free energy is the same for the two states under consideration. Therefore, $\Delta F=0$. On the other hand, the following is obtained from (II.3)

$$\frac{\partial}{\partial T}(\Delta F) = 3N\left\{\frac{1}{2}\left(\frac{\partial A}{\partial T}\right)_{T=T_m}\varepsilon^2(T_m) + \frac{1}{3}\left(\frac{\partial B}{\partial T}\right)_{T=T_m}\varepsilon^3(T_m) + \frac{1}{4}\left(\frac{\partial C}{\partial T}\right)_{T=T_m}\varepsilon^4(T_m)\right\}$$
$$+ 3N\left\{A(T_m)\,\varepsilon(T_m) + B(T_m)\,\varepsilon^2(T_m) + C(T_m)\,\varepsilon^3(T_m)\right\}\left\{\frac{\partial}{\partial T}\varepsilon(T)\right\}_{T=T_m}.$$

But, since dF has a minimum at $\varepsilon=\varepsilon(T_m)$, we have

$$A(T_m)\,\varepsilon(T_m) + B(T_m)\,\varepsilon^2(T_m) + C(T_m)\,\varepsilon^3(T_m) = 0$$

and, therefore,

$$\Delta U = 3NT_m \left| \frac{1}{2}\left(\frac{\partial A}{\partial T}\right)_{T=T_m} \varepsilon^2(T_m) + \frac{1}{3}\left(\frac{\partial B}{\partial T}\right)_{T=T_m} \varepsilon^3(T_m) + \frac{1}{4}\left(\frac{\partial C}{\partial T}\right)_{T=T_m} \varepsilon^4(T_m) \right|. \qquad \text{(II.10)}$$

2. Variation of elastic constants with temperature

In our model, we can predict the behavior of the variations with temperature of the total modulus of shear A_t which is connected to the constants of rigidity C_{11} and C_{12}, calculated for a crystal volume containing 3N transition atoms, by

$$3NA_t = \frac{3}{2}(C_{11} - C_{12}). \qquad \text{(II.11)}$$

For $T>T_m$, dF is at a minimum for $\varepsilon=0$, and A_t is the coefficient A, given by equation (II.4). Contribution A' of the conduction electrons is positive, and it varies very little with temperature. On the other hand, contribution A" of the d electrons expressed by the first two terms in (II.4), is negative, and it decreases very rapidly in absolute value as the temperature increases. For temperatures immediately above T_m, A' and A" have almost equal absolute values, and A_t is very small. On the contrary, at ordinary temperatures, A" has an absolute value of no more than one tenth of the value of A'. A_t is then nine tenths of A'. Fig. 2A shows that, just above T_m, the variations of A_t with T can be considered linear, and their extension to the left intersects the temperature axis at $T=T_0$, with T_0 very slightly less than T_m (Fig. 4). Difference T_m-T_0 is obtained from (II.7). This anomaly in the behavior of A_t has been brought out experimentally in V_3Si by Testardi, Bateman, Reed and Chirba [3].

For $T<T_m$, dF is at a minimum at a certain value $\varepsilon(T)$ of ε, different from zero. Then, A_t is no longer equal to coefficient A given by (II.4), but it is directly connected to the second order coefficient of the expansion of dF in $\varepsilon-\varepsilon(T)$. Thus, it is found that

$$A_t = A + 2B\varepsilon(T) + 3C\varepsilon^2(T) + 4D\varepsilon^3(T) \qquad \text{(II.12)}$$

where D is the coefficient of the fifth order term in (II.3), which can be written $D\varepsilon^5/5$.

For $T=T_m$, (II.8) and (II.12) show that $A_t(T_m)=A(T_m)+4D\varepsilon^3(T_m)$, which means that the modulus of shear has a discontinuity for $D\varepsilon^3(T_m)$ during the transition though it is very small, because it is proportional to $\varepsilon^3(T_m)$. This is quite consistant with the fact that

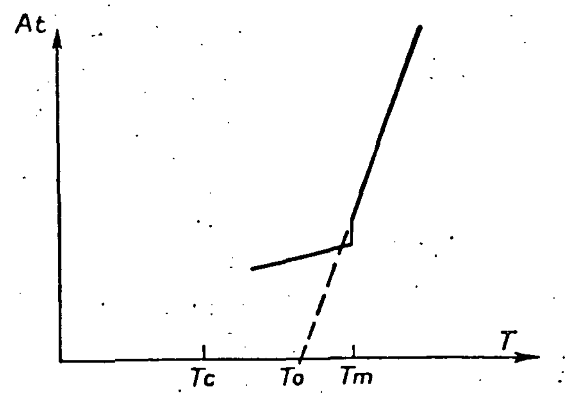

Fig. 4. Variations of modulus of shear A_t with temperature T.

the transition is of the first order.

3. Application to case of V_3Si

In V_3Si, the distortion observed by Batterman and Barrett [4] is tetragonal, with a positive value of ε. Therefore, we are in b or c of the discussion of I.2.E [6], and the number Q of electrons in the nearly empty d band per transition atom satisfies the double inequality

$$\frac{16}{3\pi^2} a^2 q^2 \frac{|E_m|}{A'} < Q < \frac{48}{5\pi^2} a^2 q^2 \frac{|E_m|}{A'};$$

which, with (I.11) expanded by Q, is also written

$$1/3 < A'/a^2 q^2 E_m^2\, n(E_F) < 3/5. \quad \text{(II.13)}$$

Morin and Maita [5] have measured the electron specific heat in V_3Si, at temperatures between 0°K and 25°K, and the value they obtain for the density of states at the Fermi level can be considered as relating to the tetragonal phase. They find a numerical value of 11 eV^{-1} per vanadium atom, with the two directions of spin taken into account. The following then is obtained from (I.45) /307

$$N_{t+}(E'_F) = 3N \times 11$$

$$= (4N/3)\left(1 - \frac{1}{2} aq\varepsilon\right) n(E_F)$$

or, by disregarding the small term $aq\varepsilon/2$,

$$n(E_F) \simeq (9/4) \times 11 \simeq 25\ \text{eV}^{-1}.$$

On the other hand, Batterman and Barrett find

$$a(1+\varepsilon)/a\left(1 - \frac{\varepsilon}{2}\right) = 1{,}0025$$

or $\varepsilon = 1.67 \cdot 10^{-3}$.

The following then is obtained from (I.11) and (I.21)

$$1{,}67 \times 10^{-3} \simeq 8aq/\pi^2 A' n(E_F). \quad \text{(II.14)}$$

Experimentally, at ordinary temperatures, it is found that [3] $C_{11} = 2.87 \cdot 10^{12}\ \text{erg} \cdot \text{cm}^{-3}$ and $C_{12} = 1.20 \cdot 10^{12}\ \text{erg} \cdot \text{cm}^{-3}$.

The crystal parameter is 2a=4.72 A. The number of vanadium atoms per cm^3 is, therefore $3N - 6(2a)^{-3} = 5.72 \cdot 10^{22}$.

From (II.21), it is then found that, at 300°K, $A_t = 27.4$ eV per vanadium atom. According to Section 2, it is then seen that there has to be $A' \simeq 30$ eV per transition atom.

Relation (II.14) involves $aq \simeq 1.57$. This leads to acknowledgement, for the unknown parameter, which is the coefficient of Slater, of the vanadium atom in the crystal, the quite reasonable numerical value $q \simeq 0.67$ A^{-1}.

The width $2|E_m|$ of the d band under consideration is, likewise, a parameter which we no not know, but, from (II.13), it is found that

$$1{,}82 \text{ eV} < 2|E_m| < 2{,}42 \text{ eV}.$$

This is a very reasonable order of magnitude for the narrowest d band, i.e., the d_{zy,x^2-y^2} band.

For example, let us take $|2 E_m| = 2.20$ eV. From (I.11), $Q=0.0593$ is then found. It is found in case b of I.2.E.

The machine calculations reported in 1 then give the following results, which can be read in Figs. 2 A,B and C:

$K \simeq 1$ eV degree^{-1} per vanadium atom
$B_0 = -0.5 \cdot 10^3$ eV per vanadium atom
$C_0 = 1.6 \cdot 10^6$ Ev per vanadium atom
$T_0 \simeq 13.3$°K.

(II.7) and (II.8) then give

$$T_m = 13.4\text{°K and } \varepsilon(T_m) \simeq 0.2 \cdot 10^{-3}.$$

The experimental value of T_m is clearly greater than 20 to 25°K. Actually, while our unidirectional model really results in a high, narrow peak for the density of states, it does not give us its exact shape in the immediate vicinity of the bottom of the band with certainty. But, for a very slightly occupied band (here, $E_F - E_m \simeq 10^{-3}$ eV), this shape begins to be of importance, as soon as the temperature rises a dozen degrees above absolute zero.

Fig. 5 represents the calculated variation of ε with temperature T. It is seen that, when T increases, initially, ε hardly varies. On the other hand, when T approaches T_m, ε begins to decrease very rapidly. This appears to be in agreement with experiment [4].

For $T=T_m$, ε only has an eighth of its value at 0°K. Therefore, the transition is only accompanied by a slight discontinuity, which is quite difficult to detect experimentally. Furthermore, the calculation gives (Fig. 2) :

$$\left(\frac{\partial A}{\partial T}\right)_{T=T_m} = K = 1\ \mathrm{eV{\cdot}deg^{-1}} \quad \text{per vanadium atom,}$$

$$\left(\frac{\partial B}{\partial T}\right)_{T=T_m} \simeq 300 \quad \text{" " "}$$

$$\left(\frac{\partial C}{\partial T}\right)_{T=T_m} = -1{,}4 \times 10^5 \quad \text{" " "}$$

Formula (II.10) then gives, for the latent heat of transformation $\Delta U \simeq 0.006$ calorie per gram atom in transition. Such a low value is difficult to measure. /308

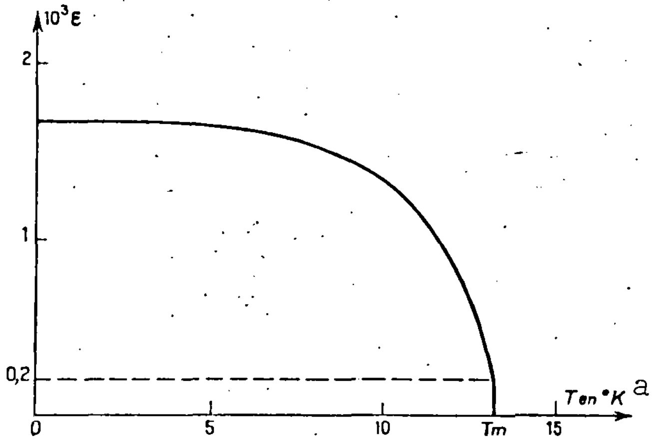

Fig. 5. Calculated variations of distortion ε with temperature T in the tetragonal phase.

Key: a. T in °K

Finally, since the transition is first order, hysteresis can be expected. With the inhomogeneities of the crystal taken into account, this undoubtedly spreads out the transition temperature. Different portions of the crystal do not undergo all the changes of structure at the same temperature. Only measurements made on a specimen which is very suitable from the metallurgical point of view have a chance of making an infinite specific heat peak appear, which corresponds to the existence of latent heat. On the other hand, if the transformation was second order, a specific heat peak of finite height, but without hysteresis, would be expected. The absence of a peak in the measured specific heat [5] is in agreement with a first order transformation.

To summarize, among the parameters which interfere in our calculations, crystal parameter a and the coefficient of shear A' at ordinary temperatures are known experimentally with certainty. On the other hand, the specific heat measurements only give us an indication of the order of magnitude of the density of states $n(E_F)$ at the Fermi level. Likewise, in reference to the values usually excepted for the transition elements, we have only a rough idea of the width $2|E_m|$ of the narrowest d band and of the coefficient of Slater q of the vanadium atom in the crystal.

By using these 5 numerical values, our calculations permit interpretation of the low temperature values and the thermal variations of two physical quantities: distortion in the tetragonal phase and a coefficient of shear. Distortion ε at low temperature has a value, which is in good agreement with that measured by Batterman and Barrett. They also allow the difference in electron specific heat in the two phases, tetragonal and cubic, to be understood.

Transition temperature T_m is only obtained in order of magnitude. Actually, different numerical tests show that it only varies slowly with band width. However, it depends greatly on details of the density of states $n(E)$, in the vicinity of the Fermi level, and these are little known.

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