Anisotropy of the thermal expansion of titanium due to proximity to an electronic topological transition

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It has been found that the thermal expansion of titanium is anisotropic in the temperature interval $10 \leqslant T < 160$ K. Specifically, the expansion coefficient is negative along the hexagonal axis and positive in the basal plane. This anisotropy is explained in terms of a particular feature of the electronic structure of titanium: proximity to electronic topological transitions.

The electronic topological transitions predicted by Lifshitz[1] rank among the most interesting effects in the physics of metals, since near such transitions one can expect to see some sharp changes and some unusual behavior of observables. Experimental activity in this field was stimulated by the prediction that such an easily measurable quantity as the thermal emf would exhibit anomalies in the course of such a transition (in alloys as well as in pure metals[2]) and by the first experimental confirmation of this prediction.[3] Since then there have been a large number experimental studies of anomalies in kinetic properties near such transitions. On the other hand, there has been essentially no study of features in thermodynamic properties. Apparently the only study in that direction has been that by Varyukhin *et al.*,[4] who observed anomalies in the specific heat in the course of an electronic topological transition in $Cd_{1-x}Mg_x$ alloys. The theory, on the other hand, predicts some obvious structural features in elastic moduli and the coefficient of thermal expansion, among other properties.[5,6]

Perhaps one of the finest predictions was the result of Ref. 7 regarding the possibility of an anisotropic thermal expansion in noncubic metals. At low temperatures, near an electronic topological transition, the thermal expansion coefficient β_i would be large and positive along one axis, while in a perpendicular direction it would be large and negative. In this letter we are reporting the first experimental observation of this anomaly in the thermal expansion, in the particular case of the hcp phase of titanium. We offer a theoretical interpretation of this anomaly.

The test sample was a titanium single crystal grown by iodine transport. The dimension of the sample in the direction perpendicular to the hexagonal axis was set at 2.115 mm by the natural faceting. The length of the sample along the hexagonal axis was 3.745 mm.

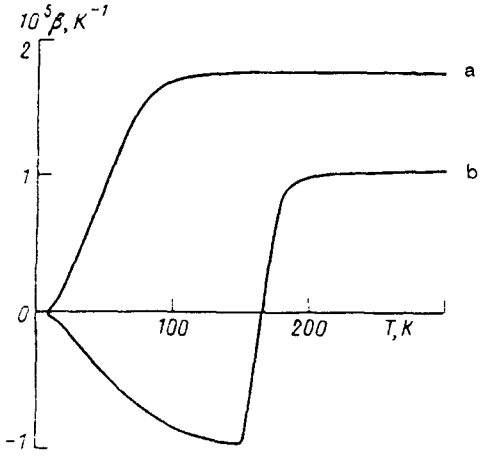

FIG. 1. Thermal-expansion coefficient of a titanium single crystal versus the temperature. a—Along the [1010] direction; b—along the [0001] direction.

A capacitance dilatometer, whose construction will be described in detail in a separate place, was used to measure the thermal expansion. Here we will simply point out that the basic elements of this dilatometer were made of pure silicon, which (as we know) has an extremely small thermal-expansion coefficient.

The experimental results are shown in Fig. 1. The thermal-expansion coefficient $\beta=(dl/dT)/l$ in the ab basal plane (curve a) has its usual form: $\beta_\perp$ is positive, it is independent of the temperature at $T>100$ K, and it falls off to zero as $T\to 0$. The behavior of the coefficient $\beta_\parallel$ along the hexagonal (c) axis is anomalous: We see a negative sign at $T<165$ K (curve b).

To interpret the results, we work from general thermodynamic expressions for β_i in biaxial crystals:[7]

$$\beta_\parallel=\frac{1}{3BB_{22}}\left[(B_{22}-2B_{12})\frac{\partial S}{\partial u_1}+(2B_{11}-B_{12})\frac{\partial S}{\partial u_2}\right],$$

$$\beta_\perp=\frac{1}{3BB_{22}}\left[(B_{22}+B_{12})\frac{\partial S}{\partial u_1}-(B_{11}+B_{12})\frac{\partial S}{\partial u_2}\right], \tag{1}$$

where S is the entropy, $du_1=d\ \ln(\Omega_0)$ is the strain related to the change in the volume per atom (Ω_0), $du_2=d\ln(c/a)$, $B_{ij}=(1/\Omega_0)(\partial^2F/\partial u_i\partial u_j)$ are the elastic moduli (F is the free energy), and $B=B_{11}-B_{12}^2/B_{22}$ is the bulk modulus. The coefficients in parentheses in (1) are positive for all metals, so $\beta_\parallel$ and $\beta_\perp$ must have different signs if $|\partial S/\partial u_2|\gg|\partial S/\partial u_1|$.

At low temperatures T, at which the electron component of the entropy is predominant, we have $S=(\pi^2/3)N(E_F)T$, where $N(E)$ is the density of electron states, and E_F is the Fermi level. Here we have

$$\partial S/\partial u_i\sim\partial N(E_F)/\partial u_i\,. \tag{2}$$

In the case of a square-root singularity in $N(E_F)$, $\delta N(E_F)\sim\eta_\pm^{1/2}$, where η is the proximity to the electronic topological transition [$\eta_\pm=\pm\eta\,\Theta(\pm\eta)$, $\Theta(x>0)=1$, $\Theta(x<0)$

$=0$], the coefficients $\beta_{\|}$ and $\beta_{\perp}$ formally diverge at the point of the transition. At moderately low temperatures, at which the S component due to long-wave vibrations [$S=12\pi^4T^3/(5\Theta)^3$, where Θ is the Debye temperature] is predominant, expression (2) remains in force, since the anomalous contributions to B_{ij} and thus to Θ are on the order of the anomalous contributions to $-N(E_F)$. The singularities in the lattice and electron components of $\beta_i(T)$ thus have identical signs and divergences of identical order in η.[5] At $T\geqslant\Theta$, at which the phonon entropy is determined by the frequencies of vibrations throughout the Brillouin zone, the singularities in S weaken[6] ($\eta^{1/2}\rightarrow\eta^{3/2}$). As a result, it can be shown[6] that the temperature dependence of the singular corrections to the phonon components of β_i are

$$\beta_i(T)=\begin{cases} A_0^i\eta^{-1/2}T^3, & T<T_s \\ A_1^i\eta^{1/2}T, & T_s<T<\Theta, \\ A_2^i\eta^{1/2}, & T<\Theta, \end{cases} \tag{3}$$

where the coefficients A_m^i depend on η and T, and $T_s\sim\Theta\eta^{1/2}$ is a characteristic temperature. The divergences of $\beta_i(T)$ at the point of the electronic topological transition thus occur as long as the relation $\beta_i\propto T^3$ holds. At small values of η, the anomalies in β_i are stronger, but they are observed in a narrower temperature interval near $T=0$.

In order to apply these general results to titanium, we carried out calculations on the electronic structure of this metal. Calculating the group velocity,[8] we found Van Hove singularities in the electron spectrum. We plotted cross sections of the Fermi surface for various electron fillings and various deformations. These calculations were carried out in the nonrelativistic version of the standard ASA-LMTO method with a Bart–Hedin exchange-correlation potential and the experimental values $c/a=1.588$ and $R=3.0727$ a.u. [$R=(3\Omega_0/4\pi)^{1/3}$ is the radius of a Wigner–Seitz sphere].

The calculations revealed that the Van Hove singularities near E_F correspond to a point lying on the ΓA line in the Brillouin zone [$\eta_1=E_{c1}-E_F=-3\times10^{-3}$ Ry; the filling of electron states which corresponds to the electronic topological transition is $n_{c_1}\equiv n(E_{c_1})\approx3.95$, $n(E_F)=4$], at the A point ($\eta_2=7\times10^{-3}$ Ry, $n_{c_2}\approx4.1$), and at a point on the ΓK line ($\eta_3=4\times10^{-3}$ Ry, $n_{c_3}\approx4.04$). The calculations show that in the first two of these cases we have $\partial E_{c_{1,2}}/\partial u_2<0$, while for the point on the ΓK line we have $\partial E_{c_3}/\partial u_2>0$ but $|\partial E_{c_{1,2}}/\partial u_2|\gg|\partial E_{c_3}/\partial u_2|$. In all three cases the relation $|\partial\eta/\partial u_2|\gg|\partial\eta/\partial u_1|$ holds ($|\partial E_{c_1}/\partial u_2|\approx4|\partial E_{c_1}/\partial u_1|$, $|\partial E_{c_2}/\partial u_2|\approx17|\partial E_{c_2}/\partial u_1|$, and $|\partial E_{c_3}/\partial u_1|\approx0$). Figure 2 shows cross sections of the Fermi surface for various values of n. We see that the electronic topological transitions at $E_F=E_{c1}$ and $E_F=E_{c3}$ correspond to a rupture of the bridge (Van Hove singularity from the saddle point), while that at $E_F=E_{c2}$ corresponds to the disappearance of the cavity (the Van Hove singularity from the maximum). The corresponding components of $N(E_F)$ are then given by

$$\begin{aligned} \delta N_1(E_F)&\sim-\sqrt{E_{c_1}-E_F}\,\Theta(E_{c_1}-E_F), \\ \delta N_2(E_F)&\sim\sqrt{E_{c_2}-E_F}\,\Theta(E_{c_2}-E_F), \\ \delta N_3(E_F)&\sim-\sqrt{E_{c_3}-E_F}\,\Theta(E_{c_3}-E_F). \end{aligned} \tag{4}$$

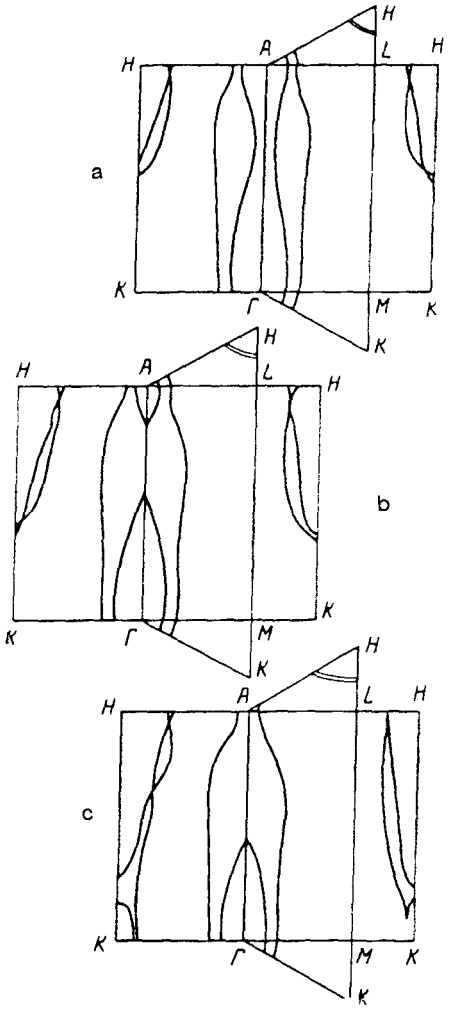

FIG. 2. Cross sections of isoenergy surfaces of titanium. a—For $n=3.90$; b—$n=4.00$ (the Fermi surface); c—$n=4.11$.

In pure titanium ($n=4$) we have $E_{c1}<E_F<E_{c3}<E_{c2}$ and thus $\partial N_1 \equiv 0$. Substituting (4) into (2), we find

$$\left(\frac{\partial S}{\partial u_2}\right)_2 \sim \frac{\partial E_{c_2}}{\partial u_2}(E_{c_2}-E_F)^{-1/2}<0,$$
$$\left(\frac{\partial S}{\partial u_2}\right)_3 \sim \frac{\partial E_{c_3}}{\partial u_2}(E_{c_3}-E_F)^{-1/2}<0. \tag{5}$$

Also using (1) and $|\partial S/\partial u_2| \gg |\partial S/\partial u_1|$, we find $\beta_\parallel<0$ and $\beta_\perp>0$. The anomalous thermal expansion in titanium can thus be attributed to its relative proximity to the electronic topological transition at the A point ($\delta n/n \simeq 0.025$) and the point on the ΓK

line ($\delta n/n \simeq 0.01$). The behavior $\beta_i(T)$ apparently agrees with the general picture summarized by expression (3), if we adopt $T_s \approx 100-150$ K ($\Theta \simeq 430$ K). A larger contribution to the anomaly apparently comes from the Van Hove singularity at the A point, since, although the Van Hove singularity at the point on the ΓK line is only half as far from E_F, the value of $|\partial E_c/\partial u_2|$ for it is smaller by a factor of 4 than that for the A point.

Anomalies in the thermal emf, apparently associated with an electronic topological transition, have been observed[9] in the alloy $Ti_{1-x}V_x$ with $x \approx 0.02$. These anomalies probably occur because the nearest Van Hove singularity at the point on the ΓK lines reaches E_F. This point furthermore influences a larger phase volume than the A point does (Fig. 2). The small value of $\partial E_c/\partial u_i$, which suppresses the contribution of this Van Hove singularity to β_i, does not influence the thermal emf. The reasons why the electronic topological transition occurs at a concentration different from $x \simeq 0.04$ are a breakdown of the rigid-band approximation in these alloys and a pronounced sensitivity of E_c to the values of c/a, which change sharply with increasing x.

Interestingly, according to the calculations above, at the value $\Delta(c/a)/(c/a) \simeq 0.02$ (corresponding to a stretching of whiskers) the Van Hove singularity associated with the A point reaches E_F, while at compressions $\Delta(c/a)/(c/a) \simeq -0.04$ this is true of the Van Hove singularity at the point on the ΓK line. Because of the one-sided nature of the Van Hove singularity, when Ti whiskers are stretched more than 2% it is possible to eliminate the contribution of the A point to β_i. The anomaly in $\beta_\parallel$ should thus decrease sharply or disappear. It would be interesting to see an experimental test of this prediction.

Corresponding anomalies in β_i associated with the electronic topological transition at the L point were predicted in Ref. 7 for $Cd_{1-x}Mg_x$ alloys with $x \geqslant 0.1$. It would also be interesting to see some corresponding experiments.

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[1] I. M. Lifshitz, Zh. Eksp. Teor. Fiz. **38**, 1569 (1960) [Sov. Phys. JETP **11**, 1130 (1960)].
[2] V. G. Vaks *et al.*, Zh. Eksp. Teor. Fiz. **80**, 1613 (1981) [Sov. Phys. JETP **53**, 830 (1981)].
[3] V. S. Egorov and A. I. Fedorov, Zh. Eksp. Teor. Fiz. **85**, 1647 (1983) [Sov. Phys. JETP **58**, 959 (1983)].
[4] S. V. Varyukhin *et al.*, Zh. Eksp. Teor. Fiz. **94**, 254 (1988) [Sov. Phys. JETP **67**, 2318 (1988)].
[5] V. G. Vaks and A. V. Trefilov, J. Phys. F **18**, 213 (1988).
[6] V. G. Vaks and A. V. Trefilov, J. Phys. Cond. Matt. **3**, 1389 (1991).
[7] V. P. Antropov *et al.*, Phys. Lett. A **130**, 155 (1988).
[8] M. I. Katsnel'son *et al.*, Fiz. Tverd. Tela (Leningrad) **32**, 470 (1990) [Sov. Phys. Solid State **32**, 272 (1990)].
[9] N. V. Bashkatov and N. L. Sorokin, Fiz. Tverd. Tela (Leningrad) **31**, 326 (1989) [Sov. Phys. Solid State **31**, 910 (1989)].

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