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#### Phase transitions and strain-induced ferroelectricity in SrTiO<sub>3</sub> epitaxial thin films

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A Landau-Ginsburg-Devonshire-type theory is used to describe the mechanical substrate effect on equilibrium states and phase transitions in SrTiO<sub>3</sub> epitaxial thin films. The misfit strain-temperature phase diagram of SrTiO<sub>3</sub> films is developed taking into account the existence of two coupled instabilities (antiferrodistortive and ferroelectric) in this crystal. It is shown that SrTiO<sub>3</sub> films remain paraelectric down to 0 K only in a narrow range of small negative misfit strains between  $-2 \times 10^{-3}$  and  $-2.2 \times 10^{-4}$ . Outside this “paraelectric gap,” the 2D clamping and straining of the film by the substrate leads to the appearance of ferroelectricity in SrTiO<sub>3</sub> films. The temperature of the ferroelectric transition increases rapidly outside the aforementioned misfit strain range.

SrTiO<sub>3</sub> is a classical example of a system with two coupled instabilities—“structural” and ferroelectric.<sup>1</sup> In a mechanically free state, bulk SrTiO<sub>3</sub> crystals undergo a cubic to tetragonal antiferrodistortive transition at 105 K (termed herein for brevity “structural transition”), which is associated with staggered rotations of the TiO<sub>5</sub> octahedra.<sup>2</sup> Despite a strong softening of the transverse optic polar mode near 0 K, the ferroelectric transition is not observed in pure SrTiO<sub>3</sub> crystals.<sup>3</sup> Therefore, this compound is regarded as an incipient ferroelectric. Recently Yamanaka *et al.*<sup>4</sup> showed that the absence of a ferroelectric phase transition in SrTiO<sub>3</sub> is not entirely due to quantum fluctuations but is in fact caused by the preceding antiferrodistortive transformation, which suppresses ferroelectric instability via the interaction between the structural order parameter and polarization. It may be expected, however, that the situation may change dramatically in SrTiO<sub>3</sub> epitaxial thin films. Indeed, a recent theoretical analysis<sup>5</sup> of equilibrium states and phase transitions in BaTiO<sub>3</sub> and PbTiO<sub>3</sub> epitaxial thin films showed that the two-dimensional (2D) clamping and straining of the film by a thick substrate may alter the type of the stable ferroelectric phase with respect to that in a bulk crystal of the same material. This substrate effect appears through a linear-quadratic coupling between the lattice strain and polarization (electrostriction). A similar coupling exists between the strain and the

structural order parameter in SrTiO<sub>3</sub>.<sup>1,6</sup> It is also clear that the interaction between the polarization and structural order parameter is renormalized in a clamped film. A difference between the sequence and type of the phase transitions in this material in thin films and bulk form can therefore be expected.

The above considerations motivated us to develop a thermodynamic theory of SrTiO<sub>3</sub> epitaxial thin films. In this paper, we report the misfit strain-temperature phase diagram of (001)-oriented single-domain SrTiO<sub>3</sub> films grown on cubic substrates. It is found that, except for a narrow range of small negative misfit strains, the ferroelectric phase transition should take place in SrTiO<sub>3</sub> films at a finite temperature. Remarkably, the 2D clamping of a thin film partly removes the suppression of the ferroelectric transition by the structural one. In contrast to the well-known stress-induced ferroelectricity in SrTiO<sub>3</sub>,<sup>1</sup> the predicted phenomenon is characterized by a rich variety of different ferroelectric phases forming in epitaxial thin films.

For bulk SrTiO<sub>3</sub> single crystals, the thermodynamic description may be developed starting from the power-series expansion of the Helmholtz free-energy density  $F$  in terms of polarization components  $P_i$  and order-parameter components  $q_i$  ( $i=1,2,3$ ).<sup>1</sup> The relevant general expression for this expansion reads

$$\begin{aligned}
F = & \alpha_1(P_1^2 + P_2^2 + P_3^2) + \alpha_{11}(P_1^4 + P_2^4 + P_3^4) + \alpha_{12}(P_1^2P_2^2 + P_1^2P_3^2 + P_2^2P_3^2) + \beta_1(q_1^2 + q_2^2 + q_3^2) + \beta_{11}(q_1^4 + q_2^4 + q_3^4) \\
& + \beta_{12}(q_1^2q_2^2 + q_1^2q_3^2 + q_2^2q_3^2) + \frac{1}{2}c_{11}(S_1^2 + S_2^2 + S_3^2) + c_{12}(S_1S_2 + S_1S_3 + S_2S_3) + \frac{1}{2}c_{44}(S_4^2 + S_5^2 + S_6^2) \\
& - g_{11}(S_1P_1^2 + S_2P_2^2 + S_3P_3^2) - g_{12}[S_1(P_2^2 + P_3^2) + S_2(P_1^2 + P_3^2) + S_3(P_1^2 + P_2^2)] - g_{44}(S_4P_2P_3 + S_5P_1P_3 + S_6P_1P_2) \\
& - \lambda_{11}(S_1q_1^2 + S_2q_2^2 + S_3q_3^2) - \lambda_{12}[S_1(q_2^2 + q_3^2) + S_2(q_1^2 + q_3^2) + S_3(q_1^2 + q_2^2)] - \lambda_{44}(S_4q_2q_3 + S_5q_1q_3 + S_6q_1q_2) \\
& - t_{11}(P_1^2q_1^2 + P_2^2q_2^2 + P_3^2q_3^2) - t_{12}[P_1^2(q_2^2 + q_3^2) + P_2^2(q_1^2 + q_3^2) + P_3^2(q_1^2 + q_2^2)] - t_{44}(P_1P_2q_1q_2 + P_1P_3q_1q_3 + P_2P_3q_2q_3),
\end{aligned} \tag{1}$$

where  $S_n$  ( $n=1,2,\dots,6$  in the Voigt matrix notation) are the lattice strains counted from the prototypic cubic state,  $c_{nl}$  are the elastic stiffnesses at constant polarization and order parameter,  $g_{nl}$  are the electrostrictive constants,  $\lambda_{nl}$  describe the linear-quadratic coupling between the strain and structural order parameter, and  $t_{nl}$  define the interaction between the polarization and order parameter under constant strain. It should be noted that in Eq. (1)  $q_i$  are set equal to the linear oxygen displacements, which correspond to simultaneous rotation of oxygen octahedra around one of their fourfold symmetry axes.<sup>6</sup>

For epitaxial thin films, a special form of the thermodynamic potential in general must be used to find equilibrium thermodynamic states of a film.<sup>5</sup> This modified potential may be derived via the Legendre transformation of  $F$  as  $\tilde{F} = F - S_3\sigma_3 - S_4\sigma_4 - S_5\sigma_5$ , where  $\sigma_n$  are the mechanical stresses in the film, defined in the rectangular reference frame with the  $x_3$  axis orthogonal to the film/substrate interface. In the particular case of a single-domain film with a mechanically free upper surface ( $\sigma_3 = \sigma_4 = \sigma_5 = 0$ ), which is considered in this paper, the energy function  $\tilde{F}$  reduces to the Helmholtz free energy  $F$ . Therefore, we may employ Eq. (1) to study the thermodynamics of SrTiO<sub>3</sub> epitaxial thin films. We consider a case of practical interest where the film is placed between two short-circuited electrodes, so that the microscopic electric field in the film is zero and depolarization-field effects should not be taken into account.

The mechanical boundary conditions of the problem must be used to determine the lattice strains involved in Eq. (1). In the present case of a single-crystalline (001) film epitaxially grown on a cubic (001)-oriented substrate, the film in-plane strains  $S_1$  and  $S_2$  should be equal to the misfit strain  $S_m$  in the heterostructure, whereas the shear strain  $S_6$  must be zero.<sup>5</sup> The remaining three strain components,  $S_3$ ,  $S_4$ , and  $S_5$ , can be found from the relations  $\partial F/\partial S_3 = \partial F/\partial S_4 = \partial F/\partial S_5 = 0$ , which follow from the boundary condition  $\sigma_3 = \sigma_4 = \sigma_5 = 0$  on the upper surface of the film. As a result, the free energy  $F$  can be reduced to a function of the misfit strain  $S_m$ , temperature  $T$ , polarization  $P_i$ , and order parameter  $q_i$ . It should be recalled that the misfit strain  $S_m$ , which is the main parameter of the epitaxial system, can be calculated as  $S_m = (b^* - a_0)/b^*$  from the effective lattice parameter  $b^*$  of the substrate and the equivalent cubic cell constant  $a_0$  of the free-standing film.<sup>5</sup>

Performing the necessary calculations, we obtain the following expression for the energy function  $F(P_i, q_i, S_m, T)$ :

$$\begin{aligned}
F = & \frac{1}{c_{11}}(c_{11}^2 + c_{11}c_{12} - 2c_{12}^2)S_m^2 + \alpha_1^*(P_1^2 + P_2^2) + \alpha_3^*P_3^2 \\
& + \alpha_{11}^*(P_1^4 + P_2^4) + \alpha_{33}^*P_3^4 + \alpha_{12}^*P_1^2P_2^2 \\
& + \alpha_{13}^*(P_1^2 + P_2^2)P_3^2 + \beta_1^*(q_1^2 + q_2^2) + \beta_3^*q_3^2 \\
& + \beta_{11}^*(q_1^4 + q_2^4) + \beta_{33}^*q_3^4 + \beta_{12}^*q_1^2q_2^2 + \beta_{13}^*(q_1^2 + q_2^2)q_3^2 \\
& - t_{11}^*(P_1^2q_1^2 + P_2^2q_2^2) - t_{33}^*P_3^2q_3^2 - t_{12}^*(P_1^2q_2^2 + P_2^2q_1^2) \\
& - t_{13}^*(P_1^2 + P_2^2)q_3^2 + t_{31}^*P_3^2(q_1^2 + q_2^2) - t_{44}P_1P_2q_1q_2 \\
& - t_{44}^*(P_1P_3q_1q_3 + P_2P_3q_2q_3),
\end{aligned} \tag{2}$$

where the renormalized expansion coefficients are given by

$$\begin{aligned}
\alpha_1^* &= \alpha_1 - \left( g_{11} + g_{12} - 2 \frac{c_{12}}{c_{11}} g_{12} \right) S_m, \\
\alpha_3^* &= \alpha_1 + 2 \left( \frac{c_{12}}{c_{11}} g_{11} - g_{12} \right) S_m, \\
\alpha_{11}^* &= \alpha_{11} - \frac{g_{12}^2}{2c_{11}}, \quad \alpha_{33}^* = \alpha_{11} - \frac{g_{11}^2}{2c_{11}}, \\
\alpha_{12}^* &= \alpha_{12} - \frac{g_{12}^2}{c_{11}}, \quad \alpha_{13}^* = \alpha_{12} - \frac{g_{11}g_{12}}{c_{11}} - \frac{g_{44}^2}{2c_{44}}; \\
\beta_1^* &= \beta_1 - \left( \lambda_{11} + \lambda_{12} - 2 \frac{c_{12}}{c_{11}} \lambda_{12} \right) S_m, \\
\beta_3^* &= \beta_1 + 2 \left( \frac{c_{12}}{c_{11}} \lambda_{11} - \lambda_{12} \right) S_m, \quad \beta_{11}^* = \beta_{11} - \frac{\lambda_{12}^2}{2c_{11}}, \\
\beta_{33}^* &= \beta_{11} - \frac{\lambda_{11}^2}{2c_{11}}, \quad \beta_{12}^* = \beta_{12} - \frac{\lambda_{12}^2}{c_{11}}, \\
\beta_{13}^* &= \beta_{12} - \frac{\lambda_{11}\lambda_{12}}{c_{11}} - \frac{\lambda_{44}^2}{2c_{44}}; \quad t_{11}^* = t_{11} + \frac{g_{12}\lambda_{12}}{c_{11}}, \\
t_{33}^* &= t_{11} + \frac{g_{11}\lambda_{11}}{c_{11}}, \quad t_{12}^* = t_{12} + \frac{g_{12}\lambda_{12}}{c_{11}}, \quad t_{13}^* = t_{12} + \frac{g_{12}\lambda_{11}}{c_{11}}, \\
t_{31}^* &= t_{12} + \frac{g_{11}\lambda_{12}}{c_{11}}, \quad t_{44}^* = t_{44} + \frac{g_{44}\lambda_{44}}{c_{44}}.
\end{aligned} \tag{3}$$

TABLE I. Nonzero components of the polarization  $P$  and the structural order parameter  $q$  in different stable phases forming in SrTiO<sub>3</sub> epitaxial thin films grown on cubic substrates.

Phase	HT	ST	SO	FTI	FTII	FOI	FOII	FOIII
$P$				$P_3$	$P_3$	$P_1$ (or $P_2$ )	$P_1$ (or $P_2$ )	$P_1$ (or $P_2$ )
$q$		$q_3$	$q_1$ (or $q_2$ )		$q_3$		$q_2$ (or $q_1$ )	$q_3$

It can be seen that, as a result of the ‘‘substrate-induced’’ renormalization, the second-order coefficients  $\alpha_i^*$  and  $\beta_i^*$  become linearly dependent on the misfit strain  $S_m$ , whereas those of fourth order simply change values.

Using Eqs. (2) and (3), we have calculated the misfit strain-temperature phase diagram of single-domain SrTiO<sub>3</sub> epitaxial films. The material parameters involved in these equations were taken from Refs. 1, 4, 7, and 8 and assumed to be temperature independent,<sup>9</sup> except for the dielectric stiffness  $\alpha_1$  and the inverse order-parameter susceptibility  $\beta_1$ . Temperature dependences of  $\alpha_1$  and  $\beta_1$  at  $T \leq 105$  K were extracted from the experimental data on temperature variations of the frequencies of the polar soft modes<sup>4</sup> and that of the order-parameter magnitude,<sup>10</sup> respectively. In order to describe in a unified manner the ‘‘quantum saturation’’ of  $\alpha_1$  and  $\beta_1$  at  $T \rightarrow 0$  K and their Curie-Weiss-type behavior at high temperatures, the dependences  $\alpha_1(T)$  and  $\beta_1(T)$  were fitted by the Barrett formula<sup>11</sup> and then extrapolated to higher temperatures.<sup>12</sup>

By calculating all of the minima of  $F(P_i, q_i, S_m, T)$  with respect to the components of the polarization and structural order parameter and then selecting the most energetically favorable phase, we determined equilibrium single-domain thermodynamic states of SrTiO<sub>3</sub> films under various strain-temperature conditions. It was found that, besides the high-temperature tetragonal (HT) phase being the distorted prototypic cubic phase, only the states with the polarization  $P$  and/or the order parameter  $q$  directed along the edges of the prototypic cubic cell may be stable in these films. They include purely ‘‘structural’’ tetragonal and orthorhombic states (denoted as ST and SO below), purely ferroelectric tetragonal and orthorhombic phases (FTI and FOI), and three ‘‘mixed’’ states (FTII, FOII, and FOIII), where both  $P$  and  $q$  differ from zero (see Table I for details). The phase diagram showing the stability ranges of these states is presented in Fig. 1.

The most remarkable feature of the calculated diagram is the presence of two wide misfit strain-temperature ranges in which SrTiO<sub>3</sub> becomes a true ferroelectric. This phenomenon is due to the coupling between the polarization and strain (electrostriction), which promotes the formation of a ferroelectric phase with an out-of-plane orientation of polarization in films grown on ‘‘compressive’’ substrates ( $S_m < 0$ ) and that with the in-plane polarization direction in the case of ‘‘tensile’’ substrates ( $S_m > 0$ ). The ‘‘paraelectric gap,’’ which separates the stability ranges of the aforementioned ferroelectric states, narrows rapidly with decreasing temperature and below about 10 K ranges from  $-2 \times 10^{-3}$  to  $-2.2 \times 10^{-4}$  (see Fig. 1).

The analysis shows that the existence of the paraelectric gap at temperatures below 30 K is caused by the interaction between the polarization and the structural order parameter. The appearance of the out-of-plane polarization component

$P_3$ , which is favored at  $S_m < 0$ , is suppressed in the presence of the nonzero order parameter  $q_3$  because the renormalized coupling constant  $t_{33}^*$  is *negative* in an epitaxial film. The situation here is similar to that in a free bulk crystal, where the coupling coefficients  $t_{11}^\sigma$  and  $t_{12}^\sigma$  under constant stress are negative.<sup>4</sup> In contrast, the renormalized constants  $t_{12}^*$  and  $t_{13}^*$  are positive in a 2D-clamped film, which explains the presence of the ferroelectric transition at zero misfit strain and in the vicinity of this point ( $S_m > -2.2 \times 10^{-4}$ ). Indeed, in the FOII and FOIII phases the polarization develops along directions orthogonal to the order parameter (see Table I) so that the discussed interaction promotes ferroelectricity in this case. (It should be noted that the coupling between  $P$  and  $q$  is relatively weak so that it does not induce new phase states and only slightly shifts the transition lines in Fig. 1, except for the ST/FTII line.)

The above results again demonstrate that the actual mechanical substrate effect on equilibrium states and phase transitions in thin films may be much more complex than predicted in earlier theoretical studies,<sup>13–15</sup> where it was supposed that the substrate-induced stresses simply shift the transition temperature and change the value of the order parameter.

Consider now the instability of the high-temperature phase in SrTiO<sub>3</sub> films. The temperature  $T_c$  of this instability varies nonmonotonically with the misfit strain, reaching a minimum value of  $T_c = 105$  K at  $S_m = 0$  (Fig. 1). The dependence  $T_c(S_m)$  here is similar to that in BaTiO<sub>3</sub> and PbTiO<sub>3</sub> films<sup>5</sup> but appears to be more complex because of the competition between two instabilities—ferroelectric and structural. At the transition lines, which limit the stability range of

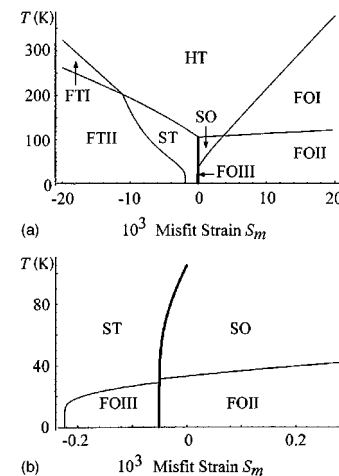


FIG. 1. Phase diagram of (001)-oriented single-domain SrTiO<sub>3</sub> thin films epitaxially grown on different cubic substrates (a) and its enlarged section near zero misfit strain (b). The second- and first-order phase transitions are shown by thin and thick lines, respectively.

the high-temperature phase, the second-order phase transitions take place so that their positions can be easily calculated from the relations  $\alpha_i^* = 0$  (HT/FOI and HT/FTI lines) and  $\beta_i^* = 0$  (HT/SO and HT/ST lines) using Eq. (3).

The phase diagram shown in Fig. 1 has two quadruple points. This contradicts the classical Gibbs rule for one-component systems, which permits, in this case, only triple points. It can be shown that, the system considered here represents an exception to the Gibbs rule. Standard arguments leading to this rule may not work in the case where lines of *second-order* phase transitions meet at a quadruple point. It is seen that it is exactly the case: the quadruple points shown in Fig. 1 are formed by lines of second-order phase transitions.

The HT/FTI and ST/FTI phase transitions should manifest themselves in a Curie-Weiss-type dielectric anomaly, which can be observed in a conventional plate-capacitor setup, where the measuring electric field  $E$  is orthogonal to the film surfaces ( $E_1 = E_2 = 0$ ,  $E_3 \neq 0$ ). On the contrary, at the HT/FOI, SO/FOII, and ST/FOIII transition lines the temperature dependence of the dielectric constant  $\epsilon_{33}$  experiences only a change of slope because the electric field does not interact with the in-plane components  $P_1$  and  $P_2$  of polarization.<sup>16</sup> These transitions, however, as well as the HT/ST and HT/SO structural transformations, may have pronounced manifestations in the temperature dependence of the internal stresses  $\sigma_1$  and  $\sigma_2$  developing in the film. To illustrate this proposition, we plotted in Fig. 2 the dependences  $\sigma_i(T)$  calculated at a representative value  $S_m = 2 \times 10^{-3}$  of the misfit strain, which was assumed to be temperature independent. [The dependence  $S_m(T)$  becomes very weak at low temperatures because of the weakness of the thermal expansion of the substrate and film]. It can be seen that phase transitions in SrTiO<sub>3</sub> thin films may be revealed experimentally by measuring the internal stresses.

We have found that the 2D clamping and straining of the film by the substrate may explain the observed drastic difference between the dielectric response of SrTiO<sub>3</sub> thin films<sup>17,18</sup> and that of a bulk crystal<sup>19</sup> at temperatures near 0 K ( $\sim 10^3$  instead of  $2.5 \times 10^4$ ). Indeed, by calculating the film dielectric susceptibility  $\chi_{33} = \partial^2 F / \partial P_3^2$  from Eqs. (2) and (3) and using the phase diagram given in Fig. 1, it can be shown that the theoretical permittivity  $\epsilon_{33}(T=0 \text{ K})$  becomes equal to the experimental value of  $\epsilon_{33} = 1300$  for a SrTiO<sub>3</sub> film grown on a LaAlO<sub>3</sub> substrate<sup>20</sup> at a reasonable misfit strain  $S_m \approx 3 \times 10^{-3}$ .

An important issue is the range of applicability of the results obtained in the paper. Since we considered here only single-domain states of single crystalline SrTiO<sub>3</sub> films, internal stresses, strains, polarization, and order parameter were

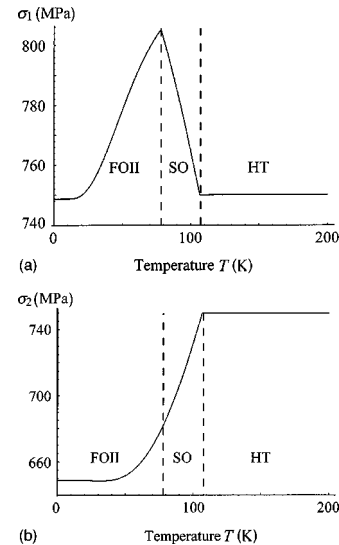


FIG. 2. Temperature dependences of the internal stresses  $\sigma_1$  (a) and  $\sigma_2$  (b) in a SrTiO<sub>3</sub> epitaxial thin film calculated in the approximation of a constant misfit strain  $S_m = 2 \times 10^{-3}$ . The phase sequence is  $HT \rightarrow SO$  ( $q_2 \neq 0$ )  $\rightarrow$  FOII ( $P_1 \neq 0$ ,  $q_2 \neq 0$ ). Note the in-plane anisotropy of the stress field in a single-crystalline film.

assumed to be homogeneous in the film. Thus, the obtained result may not be applicable for a description of inhomogeneous (polydomain or heterophase) states of the films, where domain-induced stress release is possible. However, the single-domain states determined in the paper can be used as a starting point for the analysis of the inhomogeneous states. On the other hand, under certain conditions, the effectively single-domain states of films (e.g., where the domain period is much greater than the film thickness) are energetically favorable and experimentally observed. For example, as follows from the general analysis of domain formation in ferroelectric and ferroelastic heterostructures<sup>20,21</sup> in films grown on compressive substrates ( $S_m < 0$ ), polydomain states are less energetically favorable than single-domain ones. In other cases, the domain formation may be suppressed by rapid cooling through the transition temperature range, as demonstrated experimentally by Ramesh *et al.*<sup>22</sup> In these cases, the results of the present paper can be directly applied.

To summarize, the thermodynamic theory predicts the appearance of strain-induced ferroelectricity in epitaxial SrTiO<sub>3</sub> thin films and demonstrates that their physical properties may differ drastically from those of bulk SrTiO<sub>3</sub> crystals due to the mechanical film/substrate interaction.

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<sup>9</sup>The list of the parameters of  $F$  (in cgs units, temperature in K):

$$\alpha_{11}=2.5\times 10^{-12}, \quad \alpha_{12}=1.5\times 10^{-12}, \quad \beta_{11}=1.94\times 10^{43}, \quad \beta_{12}=3.96\times 10^{43}, \\ c_{11}=3.36\times 10^{12}, \quad c_{12}=1.07\times 10^{12}, \quad c_{44}=1.27\times 10^{12}, \quad g_{11}=1.39, \quad g_{12}=-0.12, \quad g_{44}=0.27, \quad \lambda_{11}=1.3\times 10^{27}, \quad \lambda_{12}=-2.5\times 10^{27}, \\ \lambda_{44}=-2.3\times 10^{27}, \quad t_{11}=-3.74\times 10^{15}, \quad t_{12}=0.15\times 10^{15}, \quad t_{44}=7.0\times 10^{15}.$$

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$$\beta_1(T)=1.32[\coth(145/T)-\coth(145/105)]\times 10^{26}.$$

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