

Magnetic-field response of the interphase boundary dynamics in perovskite solid solutions

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Effects of magnetic-field and composition changes on the interphase boundary dynamics are considered for perovskite ferroelectric solid solutions. The width of the interphase boundary and its velocity are calculated as functions of a magnetic-field strength and the concentration of one component of the solid solution. The experimental data for $\text{Ba}_{1-n}\text{Sr}_n\text{TiO}_3$ are employed in our calculations.

I. INTRODUCTION

The perovskites are an extremely important class of materials, which may undergo a series of ferroelectric transitions with decreasing temperature.¹ The ABO_3 -type perovskites constitute an interesting group of oxide crystals with broad ranges of technologically important dielectric, piezoelectric, electro-optic, and superconducting properties.¹⁻³ In addition to the interest in the pure crystals, mixed crystals of these oxides, particularly $\text{K}(\text{Ta},\text{Nb})\text{O}_3$ (KTN) and $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ (PZT), have attracted considerable attention in the development of integrated microelectromechanical, transistor, memory, and optical devices.^{2,3} Different physical properties of the perovskite solid solutions can be adjusted by changing the concentration of their components. The dielectric properties and phase transitions in many ferroelectric perovskite crystals can be understood in terms of soft optical phonons, which involve primarily either the vibrations or rotations of the oxygen octahedra.^{1,4} The phase transitions are attributed to the condensation of these soft-modes. The delicate balance of short-range forces, favoring the paraelectric cubic phase and long-range forces favoring the ferroelectric state makes the transition sensitive to hydrostatic pressure.⁴⁻⁶ The pressure effect on the dielectric properties is well understood in terms of the soft-mode picture.⁴⁻⁶ In perovskites, pressure brings about an increase of the soft-mode frequency leading to increasing stability of the paraelectric cubic phase and a decrease of the paraelectric-ferroelectric phase transition temperature. In perovskites large pressure shifts of phase transitions were observed.⁴⁻⁶ However the majority of the pressure researches in perovskites has been devoted to the study of their static properties. Recently we have examined the pressure response of the dynamics of ferroelectric interphase boundaries in pure perovskites

and showed that this pressure effect is considerable.⁷ A strong influence of the composition on the dielectric properties of the ferroelectric solid solutions shows that concentration changes of components of solid solutions can also produce a large effect on the dynamics of interphase boundaries. On the other hand, small magnetic-field shifts of the temperature of ferroelectric phase transitions were observed in pure perovskites BaTiO_3 and KTaO_3 (tenths of a degree at 20 T).^{8,9} Despite such small shifts, we have recently shown that the magnetic-field effect on the ferroelectric interphase boundary dynamics in pure ferroelectrics may be large.¹⁰ In perovskites, an external magnetic field and a concentration change act on the phase transition temperature in opposite directions: the phase transition is shifted to higher temperatures by the magnetic-field increase and it is shifted to lower ones by increasing the concentration. Thus, in perovskites with changing stoichiometry the kinetics of the phase transitions under the influence of magnetic fields are more complicated. In this paper, we examine the concentration and magnetic-field effects on the interphase boundary dynamics in perovskite ferroelectric solid solutions. We propose a theory of such dynamics based on an exact solution of the time-dependent Ginzburg-Landau equation of motion. We use here the experimental data for the ferroelectric solid solution $\text{Ba}_{1-n}\text{Sr}_n\text{TiO}_3$.

II. MODEL

In the presence of an external magnetic field, the free-energy density of perovskite ferroelectrics in the cubic phase can be described phenomenologically by^{8,10}

$$f = f_0 + \frac{1}{2}AP^2 - \frac{1}{4}BP^4 + \frac{1}{6}CP^6 + dX^2 + eXP^2 - \frac{1}{2}gP^2H^2 - \frac{1}{2}hP^2H^4 + iXH^2 + D\left(\frac{\partial P}{\partial x}\right)^2. \quad (1)$$

Here the order parameter P is the polarization and the strain X is the external parameter. f_0 is the free-energy density for the paraelectric phase, D is the positive coefficient of the inhomogeneity term. For positive B and C , Eq. (1) describes a first-order phase transition. For negative B a second-order phase transition takes place. A tricritical point is reached if $B = 0$. The coefficient A may be assumed as a linear function of the temperature $A = A'(T - T_0)$, where T_0 is the temperature of the stability limit of the paraelectric phase. For the solid solution $(\text{Ba}_{1-n}\text{Sr}_n)\text{TiO}_3$ the difference between the ferroelectric-paraelectric phase transition temperature T_c and T_0 decreases with increasing Sr concentration n . We can present the coefficient B as follows: $B = b(n_t - n)$, where b does not depend on the Sr concentration n ; in the pure BaTiO_3 $n = 0$, i.e., $B_0 = bn_t$, where n_t is the tricritical concentration. Because of symmetry, only even powers in the magnetic field enter. From the minimization conditions $\frac{\partial f}{\partial P} = 0$ and $\frac{\partial f}{\partial X} = 0$ it follows that the change in transition temperature is also proportional to even powers in the magnetic field. The magnetic-field shift of the phase transition occurs due to the magnetoelectric effect and its field dependence is described by the sum of the quadratic and quartic power terms in H according to experimental data.^{8,9} The sign of the magnetoelectric terms in (1) is determined by the direction of the magnetic-field shift of the transition temperature. In BaTiO_3 and KTaO_3 the increase in the magnetic field leads to the increase in the phase transition temperature.^{8,9} The reason for the growth of the phase transition temperature with increasing magnetic-field strength is probably the magnetic-field-induced increase of the polarization as a result of the magnetoelectric effect.

A possible microscopic origin of the magnetic-field effect on the polarization follows from the recent first-principles calculations for BaTiO_3 and PbTiO_3 ,¹¹ which have shown that the ferroelectric state is determined by the Ti-O hybridization: if the Ti-O hybridization is inhibited, the ferroelectric instability disappears and the cubic paraelectric phase is most stable, i.e., hybridization between the Ti cation and O is essential to weaken the short-range repulsions and allow the ferroelectric transition. Since the lowest unoccupied state of Ti^{4+} is a d state, this allows for d hybridization with the O that softens the Ti-O repulsion and enables the ferroelectric state. The magnetic field softens the Ti-O repulsion and thus shifts the phase transition to higher temperatures. This tendency is opposite of the pressure effect. Pressure decreases the interionic distances, and the influence of the magnetic field may be simulated on the increase of the interionic distances.

At atmosphere pressure, the ferroelectric first-order phase transition takes place in pure BaTiO_3 at $T = 408$ K.¹ The increase of the Sr concentration leads to the

changeover of the phase transition: the first-order transition transforms into the second-order one. The tricritical concentration of Sr, n_t is 0.6.¹² Let us show that the magnetic field cannot change the transition order in this case. Since there is no magnetostriction in a diamagnetic material like BaTiO_3 , the direct coupling of the magnetic field to the polarization dominates the influence of magnetostriction. In a ferroelectric material such as BaTiO_3 , the discontinuous behavior of the order parameter at the first-order ferroelectric-paraelectric phase transition can be understood in terms of an electrostrictive coupling between the displacement of the ferroelectrically active ion and the elastic strain of the crystal.¹³ In the lattice-dynamics terms, this can be thought of as anharmonic coupling between the soft transverse-optic mode and the acoustical modes of the crystal. It has been shown¹⁴ that, if sufficiently high hydrostatic pressure is applied to BaTiO_3 , the first-order transition becomes changed in second order. This phenomenon, occurring in perovskite solid solutions, is similar to decreasing the concentration of one component. One of the mechanisms,¹⁵ by which the tricritical point can be reached in perovskite ferroelectrics, is a reduction of the electrostrictive coupling by high pressures or by alloying. The magnetic field cannot affect elastic strains because of the absence of magnetostriction. For this reason, it does not change the order of the phase transition but shifts its temperature. This means that the coefficient B in (1) does not depend on the magnetic-field strength. In the present case, the electrostrictive coupling term is reduced by alloying. Thus, the tricritical point occurs here as disorder is introduced into BaTiO_3 structure, by the addition of definite amounts of SrTiO_3 .

At a constant pressure and temperature, the interphase boundary separating the paraelectric and ferroelectric phases exists at the concentration range $n_0 < n < n^*$, where n^* is the concentration corresponding to the stability limit of the ferroelectric phase and n_0 is the concentration corresponding to the stability limit of the paraelectric phase; $n^* < n_t$. The phase transition concentration n_c is the concentration at which depths of minima of the paraelectric and ferroelectric phases are equal. By changing the Sr concentration n one can induce the motion of the ferroelectric interphase boundary. These dynamics are described in terms of the time evolution of the polarization P :

$$\frac{\partial P}{\partial t} = -\Gamma \frac{\delta F}{\delta t}. \quad (2)$$

Γ is the kinetic coefficient which is assumed to depend noncritically on temperature, pressure, concentration, and magnetic field. F is the bulk free energy. The functional derivative $\frac{\delta F}{\delta P}$ tends to restore the value P to its thermal value. When displaced away from the equilibrium state, by changing the concentration of Sr, the system will relax back. The kinetics of the relaxation towards equilibrium may be described in terms of the time evolution of the polarization Eq. (2). The corresponding equation of motion is as follows:

$$\Gamma(AP - BP^3 + CP^5 - gPH^2 - hPH^4) + \frac{\partial P}{\partial t} - 2\Gamma D \frac{\partial^2 P}{\partial x^2} = 0, \quad (3)$$

where A is the coefficient, which is renormalized by the strain. Using $s = x - vt$, we obtain

$$2\Gamma D \frac{d^2 P}{ds^2} + v \frac{dP}{ds} - \Gamma(aP - BP^3 + CP^5) = 0, \quad (4)$$

here $a = A - gH^2 - hH^4$. The solution of Eq. (4) for the interface boundary conditions has the kink form¹⁶

$$P = \frac{P_0}{\sqrt{1 + \exp(\frac{s}{\Delta})}}, \quad (5)$$

where P_0 is the equilibrium value of polarization

$$P_0^2 = \frac{B}{2C}(1 + \sqrt{1 - 4\alpha}), \quad (6)$$

and Δ is the width of the interphase boundary given by

$$\Delta = \frac{(3DC)^{\frac{1}{2}}}{B\sqrt{1 - 2\alpha + \sqrt{1 - 4\alpha}}}, \quad (7)$$

which moves with the velocity v , given by

$$v = \frac{\sqrt{2D}}{3} \frac{\Gamma B}{\sqrt{C}} \frac{(8\alpha - 1 - \sqrt{1 - 4\alpha})}{\sqrt{1 - 2\alpha + \sqrt{1 - 4\alpha}}}, \quad (8)$$

where $\alpha = \frac{gC}{B^2}$. Equation (5) describes the kink profile of the moving interphase boundary separating the paraelectric and ferroelectric phases.

The experimental data used here for calculations are $A'_0(n=0) = 7.41 \times 10^{-5} \frac{1}{K}$ (Ref. 17) [$A'_0(n=0)$ denotes the coefficient A'_0 for the pure barium titanate, i.e., when the Sr concentration n equals zero], $B_0 = 6.8 \times 10^{-13} \text{ cm sec}^2/\text{gr}$,¹² $n_t = 0.6$,¹² $C = 2.28 \times 10^{-22} \text{ cm}^2 \text{ sec}^4/\text{gr}^2$,¹⁷ $\frac{dT_0}{dn} = -358 \text{ K}/n_{\text{Sr}}$,¹² $\frac{A'_0 C}{B^2} g = 6.27 \times 10^{-4} \text{ K}/T^2$,⁸ $\frac{A'_0 C}{B^2} h = 6.28 \times 10^{-7} \text{ K}/T^4$,⁸ $D = 3.35 \times 10^{-16} \text{ cm}^2$,¹⁶ $\Gamma = 10^{10} \text{ sec}^{-1}$ (Refs. 18 and 19) (we use the value of Γ for PbTiO_3 and NaNbO_3 , as this coefficient has not been measured for BaTiO_3 and SrTiO_3). $D(n)$ is proportional to the square of the lattice parameter.¹⁶ Variations of Δ and v are primarily determined by $T_0(n)$ and $B(n)$, while the dependence of $D(n)$ is negligible.

III. RESULTS

In Fig. 1, the interphase boundary width Δ increases with increasing concentration of Sr n in $\text{Ba}_{1-n}\text{Sr}_n\text{TiO}_3$ at $\Delta T = T_0^0 - T = 25 \text{ K}$; T_0^0 is the stability limit of the paraelectric phase in pure BaTiO_3 [$T_0^0 = 293 \text{ K}$ (Ref. 1)]. The maximal increase of width is approximately equal to 2. With increasing ΔT , the width increases but remains finite. In Fig. 2, in pure BaTiO_3 at $\Delta T = T - T_0^0 = 8 \text{ K}$ (curve 1) the interphase boundary width Δ decreases with increasing magnetic field H . The decrease

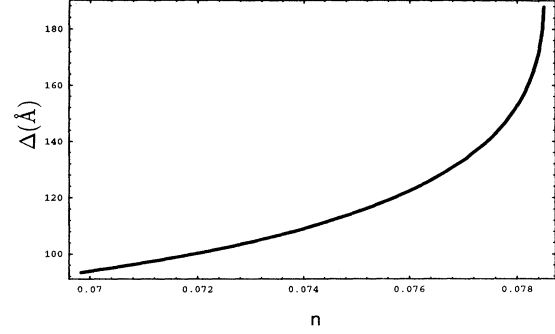


FIG. 1. The interphase boundary width Δ (Å) as a function of the Sr concentration n in $\text{Ba}_{1-n}\text{Sr}_n\text{TiO}_3$ at $\Delta T = T_0^0 - T = 25 \text{ K}$. T_0^0 is the limit stability temperature of the paraelectric phase in the pure BaTiO_3 .

of ΔT leads to change of the slope of the curve showing the concentration dependence of the interphase boundary width: it transforms into a straight line (see plot 2 at $\Delta T = 6.85 \text{ K}$). The magnetic-field behavior of the width obtained here is essentially different from the one calculated in Ref. 10, where the interface width increases with increasing magnetic field.

In Fig. 3, the interphase boundary velocity v is shown as a function of the Sr concentration n in $\text{Ba}_{1-n}\text{Sr}_n\text{TiO}_3$ at $\Delta T = 5 \text{ K}$. We see that a change of n above or below the phase transition concentration n_c induces the interface motion towards the paraelectric or ferroelectric phase, respectively. Thus, the ferroelectric phase grows at the expense of the paraelectric phase or vice versa. At $n = n_c$ phase transition concentration the interphase boundary stops because of the equality of the free-energy densities in the two phases. At $n = n_c$ the interphase boundary changes the direction of its motion. On moving away from the phase transition concentration n_c the velocity increases. In Fig. 4, the interphase boundary velocity v is shown as function of the magnetic field H at $\Delta T = 8 \text{ K}$ (curve 1). H_c is the magnetic field intensity, for which depths of free-energy wells are equal, thus H_c

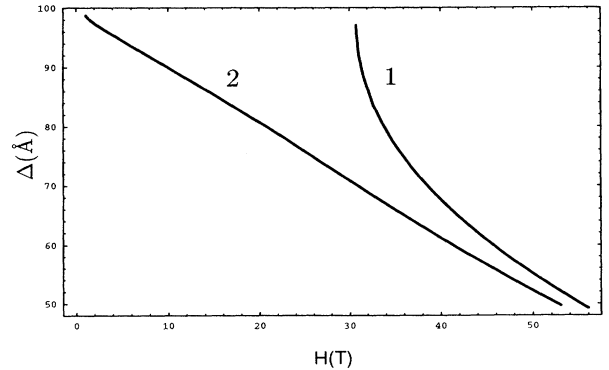


FIG. 2. The interphase boundary width Δ in Å as a function of the magnetic field H (T) in pure BaTiO_3 , curve 1 corresponds to $\Delta T = T - T_0^0 = 8 \text{ K}$, curve 2 corresponds to $\Delta T = 6.85 \text{ K}$.

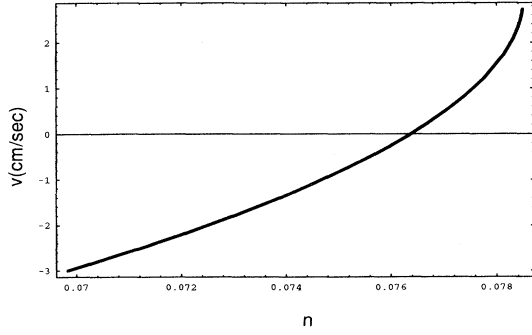


FIG. 3. The interphase boundary velocity v in cm/sec as a function of the Sr concentration n in $\text{Ba}_{1-n}\text{Sr}_n\text{TiO}_3$ at $\Delta T = 5$ K.

is the point of the phase transition in magnetic field for which $v = 0$. The velocity v increases on moving away from H_c . At $H = H_c$ the direction of motion of the interphase boundary changes. The slope of the velocity as function of the magnetic field H is determined by the temperature difference ΔT : the velocity curve changes the sign of its curvature with decreasing ΔT (see curve 2 at $\Delta T = 6.85$ K). This means that the temperature decrease hampers the growth of the paraelectric phase. The growth rate decreases with decreasing temperature. At constant concentration and temperature, the interphase boundary exists in the range $H_0 > H_c > H^*$. H_0 is the magnetic-field strength corresponding to the stability limit of the paraelectric phase. H^* is the magnetic-field strength corresponding to the stability limit of the ferroelectric phase. At constant magnetic field, the conditions for the existence of the interphase boundary are $n_0 < n_c < n^*$ and $T_0 < T_c < T^*$ (T^* is the temperature of the stability limit of the ferroelectric phase) and this leads to the change of the interphase boundary dynamics parameters. This change is opposite to the mentioned above. The concentration increase of 9% for $n > n_c$ leads to a 300% increase in velocity. An increase of the magnetic

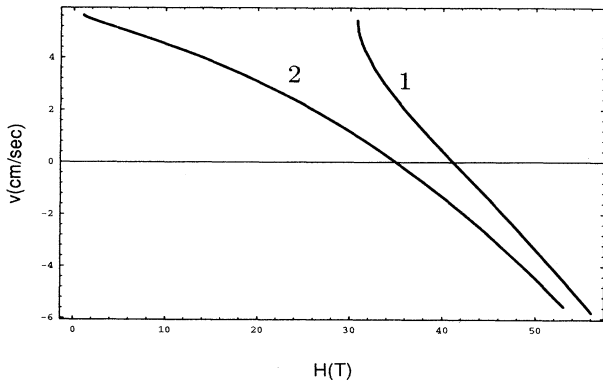


FIG. 4. The interphase boundary velocity v in cm/sec as a function of the magnetic field H (T) in pure BaTiO_3 (curve 1 corresponds to $\Delta T = T - T_0^0 = 8$ K, curve 2 corresponds to $\Delta T = 6.85$ K).

field leads to motion of the interphase boundary implying the growth of the ferroelectric phase at the expense of the paraelectric one. Decrease in the magnetic field leads to motion of the interphase boundary implying the growth of the paraelectric phase at the expense of the ferroelectric one. It follows from Fig. 4 that the increase in the magnetic-field strength up to 20 T causes a threefold velocity decrease, while the phase transition temperature increases only by 0.3 K at the same field range. Thus, the magnetic field induces a 300% change of the velocity in comparison with the slight shift of several tenths percent of the phase transition temperature. The resulting change in the width, about 15%, is large compared with the slight shift of the phase transition temperature. We conclude that the effect of the velocity with the magnetic field is the opposite to that described in Ref. 10. This large magnetic-field effect takes place close to phase transition within the range of coexistence of metastable and stable phases. In this region, the system is very sensitive to external conditions, because a slight variation of external fields leads to a substantial change of the curvature of free-energy densities as function of polarization P , and it modifies the depth of their absolute and relative minima of the coexisting phases. In the vicinity of the phase transition point one of the phases becomes metastable and the other phase becomes stable. In Fig. 4 we show the effect of critical slowing down in the interphase boundary motion: the velocity is equal to zero at the phase transition point. Thus, any change of the external magnetic field results in substantial variation of the interphase boundary velocity in the vicinity of the phase transition point. The interphase boundary velocity equals zero at this point and therefore the strong dynamic effect is caused by the first-order nature of the phase transition. As is known in the study of relaxational phenomena,¹ observations of critical slowing down are very effective in the study of phase transitions. For this reason, measurements of the interphase boundary dynamics under magnetic-field influence can be more informative than static measurements in external magnetic field. All the relative changes of the interphase boundary velocity caused by the magnetic field and composition are large and they may be detected using a polarization microscope.^{18,19}

Let us calculate the surface tension of the interphase boundary σ as an additional free energy per unit area

$$\sigma = \int_{-\infty}^{+\infty} \left(\frac{\partial P}{\partial x} \right)^2 dx. \quad (9)$$

Using (5) and integrating it in (9) we obtain

$$\sigma = \frac{DP_0^2}{4\Delta}. \quad (10)$$

We can check our calculations by comparing it with the experimental value for the surface tension of the interphase boundary for BaTiO_3 obtained in Ref. 20 at $T = T_c$: $\sigma = 0.260$ erg/cm². Using the above D and Eq. (10), we obtain $\sigma = 0.282$ erg/cm² at the same temperature ($T = T_c$ or $\alpha_c = \frac{3}{16}$). This is additional evidence that the mean-field approximation works well in this case. The mean-field approximation is also reasonable for the

temperature-induced interphase boundary dynamics in ferroelectric and antiferroelectric perovskites, as shown by experiments.^{21,22} Using (6) and (7) we have

$$\sigma = \frac{D^{\frac{1}{2}} B_0^2}{8\sqrt{3}C^{\frac{3}{2}}} \left(1 - \frac{n}{n_t}\right)^2 (1 + \sqrt{1 - 4\alpha}) \times (\sqrt{1 - 2\alpha} + \sqrt{1 - 4\alpha}). \quad (11)$$

It is seen, that at the tricritical point $n = n_t$ the interphase boundary disappears and $\sigma = 0$. In Fig. 5(a), the surface tension of the interphase boundary σ is shown as a function of n at $H = 50$ T (1) and at $H = 15$ T (2). The decreasing tendency takes place in the two cases. In Fig. 5(b), the surface tension is shown as a function of H . Curves 1 and 2 correspond to the 1 and 2% concentration of Sr, respectively. It is seen that the surface tension is an increasing function of H . These H and n dependences of σ are described by the corresponding behavior of the interphase boundary width following from (7) and (10).

It is interesting to consider the strongly metastable states, i.e., the behavior of the system near the limits of the phase coexistence ($\alpha \ll 1/4$ and $\alpha \sim 1/4$). For $\alpha \ll 1/4$ the width $\Delta \sim (1 + \alpha)/(n_t - n)$, $v \sim (n - n_t)$, and $\sigma \sim (n_t - n)^2$. This means that the velocity and surface tension are almost independent of temperature and magnetic field. For the other limited case ($\alpha \sim 1/4$) the width $\Delta \sim 1/(n_t - n)1/\alpha^{0.5}$. It is substantially different from the first case and the interphase boundary moves in the opposite direction: $v \sim (n_t - n)\alpha^{0.5}$ and $\sigma \sim (n_t - n)^2\alpha^{0.5}$. It should be noted that the diagrams of the phase growth constructed here substantially reflect the peculiarities of the solid solution and its response to the external magnetic field. The slope of the T -, n -, and H -velocity is a very sensitive function of the material under study. Thus the magnetic-field concentration diagrams can indicate the properties of ferroelectric solid solutions.

Our main conclusion is that the interphase boundary dynamics are much more sensitive to magnetic fields and composition changes than the static dielectric properties. This is why the measurements on the interphase boundary dynamics may be very informative. Some experiments on the thermoinduced dynamics of ferroelectric and antiferroelectric interphase boundaries in perovskites have been carried out in recent years.^{18,19}

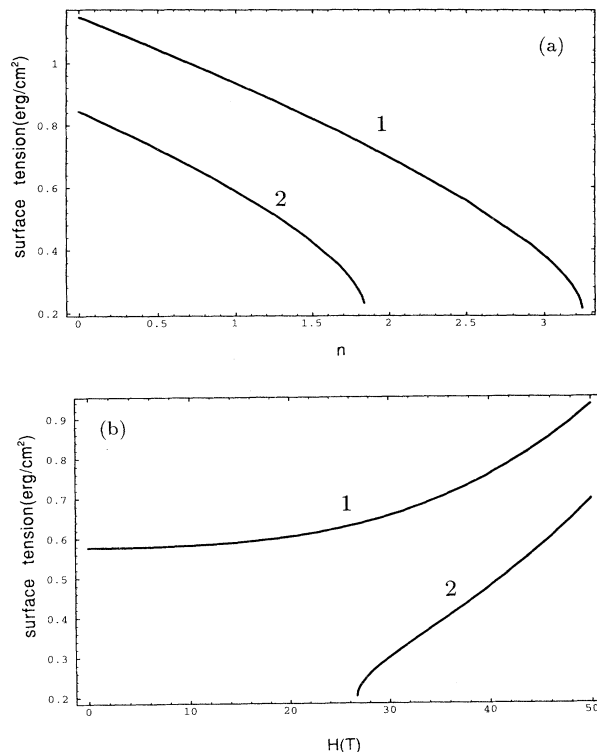


FIG. 5. The surface tension of the interphase boundary σ in erg/cm^2 at $T = T_c$ in $\text{Ba}_{1-n}\text{Sr}_n\text{TiO}_3$: (a) as a function of concentration n , the upper and lower curves correspond to calculations at magnetic field 50 and 15 T, respectively; (b) as function of magnetic field H in T, at concentrations 1 and 2%, which correspond to the upper and lower curves, respectively.

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