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Phenomenological theory of size effects in ultrafine ferroelectric particles of lead titanate

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A new phenomenological model is proposed and discussed to study size effects on the first-order ferroelectric phase transition of lead titanate ferroelectric particles. This model, by taking size effects on the phenomenological Landau-Ginzburg-Devonshire coefficients into consideration, can successfully explain the observed size effects on the Curie temperature, c/a ratio, and thermal and dielectric properties of lead-titanate-type ferroelectric particles. Theoretical and experimental results for $PbTiO_3$ fine particles are compared and discussed. The relationship between the current model and the model of Zhong *et al.* [Phys. Rev. B **50**, 698 (1994)] is also discussed. [S0163-1829(99)10637-4]

I. INTRODUCTION

Size effects on ferroelectric materials have been studied both experimentally[1–6] and theoretically.[7–13] Experimental results all showed that there are strong size effects on ferroelectric materials. All the experiments done on $PbTiO_3$, $BaTiO_3$, and $PbZrO_3$ particles show that the Curie temperature, tetragonality (c/a ratio), latent heat, and soft-mode frequency all decrease with decreasing particle size. Theoretically, Cottam, Tilley, and Zeks[7] investigated the occurrence of surface modes in semi-infinite ferroelectric materials. Three different approaches were used: (1) a microscopic pseudospin theory based on the Ising model in a transverse field, (2) a macroscopic Landau theory in which surface effects can be introduced phenomenologically, and (3) a polariton model appropriate for the very-long-wavelength region. Existence conditions and dispersion relations were deduced for the localized surface modes, which were predicted by all three methods. The results were illustrated by means of numerical examples. Methods (1) and (2) gave rise to similar results within certain limits, and a formal relationship between these two approaches was established. Tilley and Zeks[8] also discussed phase transitions in ferroelectric thin films using a theoretical model based on the Landau-Devonshire expansion. A surface is characterized by an extrapolation length δ, the negative of the logarithmic derivative of the order parameter at the surface. For negative δ, the critical temperature T_c of a film is increased above the bulk value, while for positive δ it is decreased. It was shown that depolarization effects further decrease T_c in general. Using this theory, Tilley and Zeks[8] discussed the thickness effects on the second-order ferroelectric-paraelectric phase transition in ferroelectric thin films. By introducing a sixth-order term, Scott *et al.*[14] discussed the thickness dependence of first-order ferroelectric-paraelectric phase transitions in ferroelectric thin films.

A Landau-type phenomenological theory for a size-driven phase transition in ferroelectric particles of $BaTiO_3$ and $PbTiO_3$ was clearly demonstrated by Zhong and co-workers,[9–13] taking the surface and nonequilibrium energy into consideration and the introduction of a surface extrapolation length δ. The model can be used for some particles having a simple geometry, such as thin films and spherical and cylindrical particles. It may be solved numerically. For spherical ferroelectric particles, we may assume uniaxial polarization, the magnitude of which depends only on the radius. Contrary to the case of thin films, the extrapolation length was shown to be size dependent. The size-dependent phase transitions have the same order as the temperature-driven phase transitions. The polarization decreases with decreasing particle size and eventually disappears (a size-driven phase transition); i.e., the Curie temperature decreases with decreasing particle size and reaches zero at the critical size. The calculated size dependence of T_c for $PbTiO_3$ and $BaTiO_3$ was said to be in excellent agreement with the experimental results for sol-gel- (SG-) derived powders.

This model[9] successfully explains the size effects on ferroelectricity and the phase transition temperature, but fails to explain the thermal properties of $PbTiO_3$ and $PbZrO_3$ fine particles. All the experimental results on $PbTiO_3$ (Refs. 2 and 6) and $PbZrO_3$ (Ref. 5) phase transitions showed that the entropy jump dropped sharply with decreasing particle size, but the calculated value[15] showed a small increase with decreasing particle size based on the model of Zhong *et al.*[9] This forces the calculated latent heat to decrease more slowly than the Curie temperature, which contradicts the experimental results. The results for $PbTiO_3$ ultrafine particles showed that as the particle size decreases from 1 μm to 23 nm, the Curie temperature decreases from 493 to 477 °C, a drop of only 16 °C, but the latent heat decreases from 1740 to 61 J/mol, which is a much larger percentage decrease. Curve fitting showed that the relationship between the size and latent heat was very close to exponential.[15] This model failed because the phenomenological coefficients were assumed to be size independent. Careful comparison with experimental results implies that, in order to explain the size effect on latent heat and entropy jump of phase transition, the size effect on the phenomenological coefficients has to be taken into consideration.

In this paper, a model derived by the authors is proposed. The relationship between our model and the model of Zhong *et al.* is also discussed and results for the physical properties referred to above are given.

II. MODEL

The size dependence of the phenomenological coefficients was already observed in experiments. Basceri *et al.*[16] reported that the first-term coefficient of the Landau-Ginsberg-Devonshire (LGD) power series was the thickness dependence for barium strontium titanate (BST) ferroelectric thin films. For ferroelectric particles such as $PbTiO_3$, which have a first-order phase transition, it was necessary to take into account the size dependence of both the first- and second-term coefficients for the LGD power series in order to explain the experimental results. After careful study of the experimental data for $PbTiO_3$, it was found that if the phenomenological coefficients are assumed to be size dependent and have the following relation, good agreement with experimental results was obtained:

$$G=\frac{1}{2}\alpha(T,d)P^2+\frac{1}{4}\beta(d)P^4+\frac{1}{6}\gamma P^6, \tag{1}$$

$$\alpha(T,d)=\alpha_0(T-T_{0\infty})+\frac{A}{d-D_s}, \tag{2}$$

$$\beta(d)=\beta_\infty \exp\left(-\frac{B}{d}\right), \tag{3}$$

assuming γ [Eq. (1)] is size independent. Equations (2) and (3) are derived from the empirical formula for size effects on the Curie temperature and the latent heat of $PbTiO_3$ fine particles, respectively. Here β_∞ is the value of β for bulk crystals and A and B are constants derived from the experimental values. For $PbTiO_3$, $A=0.04\,\mathrm{J\,m^2\,C^{-2}}$ and $B=80\,\mathrm{nm}$. D_s is a special particle size very close to the critical size and obtained from experiment. $D_s=8.8\,\mathrm{nm}$ for $PbTiO_3$.[2] $T_{0\infty}$ is the Curie-Weiss temperature of the bulk materials, and d is the particle size. Other parameters for lead titanate are $\alpha_0=2.79\times10^5\,\mathrm{J\,m\,C^{-2}\,K^{-1}}$, $\beta_\infty=-1.62\times10^9\,\mathrm{J\,m^5\,C^{-4}}$, and $\gamma=4.23\times10^{11}\,\mathrm{J\,m^9\,C^{-6}}$.[17]

A. Microscopic explanation

Following Devonshire's formulas,[18] the phenomenological coefficients α and β are related to the crystal structure and force constants. From the experimental results for $BaTiO_3$, $PbTiO_3$, and $PbZrO_3$ fine particles[2,5,6,19] the measured c/a ratio decreases with decreasing particle size. This will change the force the ions feel. The dependence of the force constants on particle size was also shown by the soft-mode measurements. Raman scattering on $PbTiO_3$ (Ref. 2) showed the soft mode decreasing sharply with decreasing particle size. Since the force constants change with particle size, the phenomenological constants α and β should also be size dependent.

B. Macroscopic explanation

According to Tilley and Zeks[8] and Zhong *et al.*,[9] the surfaces of ferroelectric thin films and particles are different from the inner part of the particle. The surface region has different polarization and dielectric constant. The free energy of the whole system can be expressed as a sum of surface and bulk terms:

$$\begin{aligned}G=G_{\text{surface}}+G_{\text{bulk}}&=\left(\frac{1}{2}\alpha_{\text{surface}}P_{\text{surface}}^2+\frac{1}{4}\beta_{\text{surface}}P_{\text{surface}}^4+\frac{1}{6}\gamma_{\text{surface}}P_{\text{surface}}^6\right)+\left(\frac{1}{2}\alpha_{\text{bulk}}P_{\text{bulk}}^2+\frac{1}{4}\beta_{\text{bulk}}P_{\text{bulk}}^4+\frac{1}{6}\gamma_{\text{bulk}}P_{\text{bulk}}^6\right)\\&=\frac{1}{2}\alpha_{\text{effective}}P_{\text{effective}}^2+\frac{1}{4}\beta_{\text{effective}}P_{\text{effective}}^4+\frac{1}{6}\gamma_{\text{effective}}P_{\text{effective}}^6.\end{aligned} \tag{4}$$

The ions near the surface will feel a different force than those at the inner part of the crystal. The phenomenological coefficient for the surface will be different from that for the bulk material. When the particle is very large, the surface effects can be neglected and $\alpha_{\text{effective}}$, $\beta_{\text{effective}}$, and $\gamma_{\text{effective}}$ will equal their bulk values. On the other hand, they will approach the surface values when the particle size is very small.

III. SIZE EFFECT ON FERROELECTRIC PROPERTIES BASED: OUR MODEL

Based on the assumption of a size dependence of the phenomenological coefficients, our model is now formulated and used to predict the size effects on the ferroelectricity of spherical particles. All the calculations are based on $PbTiO_3$ to allow the theoretical calculations to be compared with the experimental results. Note that, so far, no distinction has been made in the size effect theory between ferroelectric and antiferroelectric phase transitions.

A. Size-driven phase transition

From Eq. (1), the spontaneous polarization P_s, phase transition temperature T_c, and spontaneous polarization at T_c (P_{sc}) can be written as

$$P_s^2=\frac{-\beta(d)+\sqrt{\beta(d)^2-4\alpha(T,d)\gamma}}{2\gamma}, \tag{5}$$

$$T_c=T_{0\infty}-\frac{A}{(d-D_s)\alpha_0}+\frac{3\beta(d)^2}{16\alpha_0\gamma}, \tag{6}$$

$$P_{sc}^2=-\frac{3\beta(d)}{4\gamma}. \tag{7}$$

Substituting Eq. (5) into Eq. (1) and taking $T=0\,\mathrm{K}$, the free energy as a function of d can be obtained. Figure 1(a) shows the theoretical results. Clearly, there exists a size-driven phase transition and a critical size d_c, below which polarization cannot be established in the particle. The spontaneous polarization P_s at $T=0\,\mathrm{K}$, as a function of particle size, is shown in Fig. 1(b). It has the characteristic of a first-order phase transition; the spontaneous polarization jumps to zero where the particle size reaches the critical size d_c. The size dependence of the phase transition temperature, calculated according to Eq. (6), is compared with experimental values

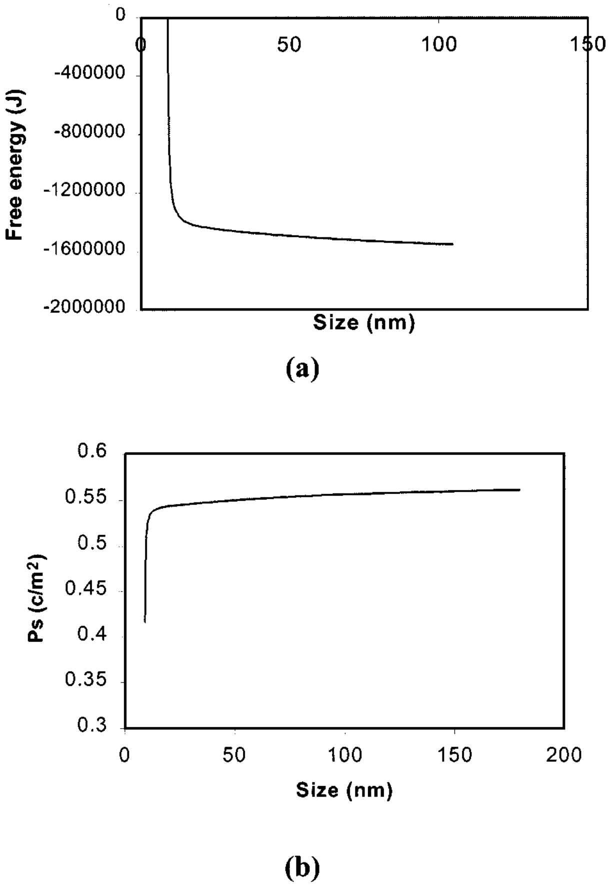

FIG. 1. Size dependence of the free energy and spontaneous polarization.

in Fig. 2. Note that the calculated temperature is renormalized to 766 K when $d=\infty$. The agreement is very good, and the Curie temperature has a significant drop only near the critical size.

B. Size effect on the latent heat and entropy change

The discontinuous change in polarization causes a discontinuous change in entropy. The entropy jump ΔS at T_c can be written as

$$\Delta S(d)=\frac{1}{2}\alpha_0 P_{sc}^2=\frac{3\alpha_0\beta(d)}{8\gamma}. \tag{8}$$

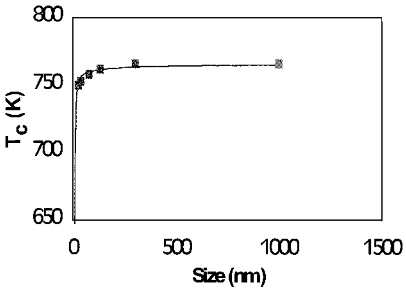

FIG. 2. Size dependence of the Curie temperature.

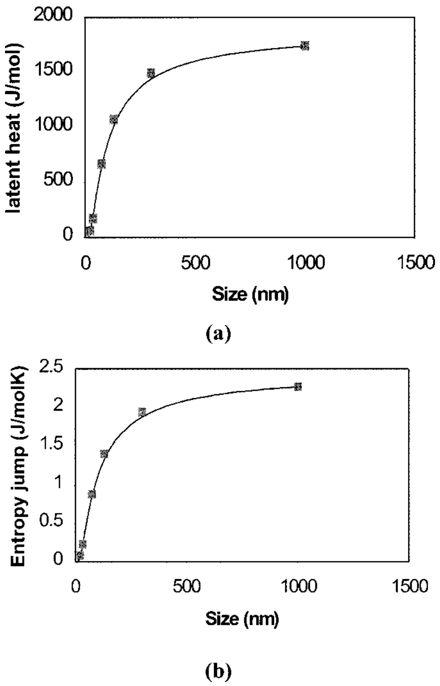

FIG. 3. Size dependence of the latent heat and entropy jump at the Curie temperature.

The resulting latent heat is

$$\Delta Q(d)=T_c\Delta S=\left(T_0-\frac{A}{(d-D_s)\alpha_0}+\frac{3\beta(d)^2}{16\alpha_0\gamma}\right)\frac{3\alpha_0\beta(d)}{8\gamma}. \tag{9}$$

Figure 3 shows the size effect on the entropy and latent heat. Note the calculated value of $\Delta S(d=\infty)$ is renormalized 2.3 $\mathrm{J\,mol^{-1}\,K^{-1}}$ and $\Delta Q(d=\infty)$ is renormalized to 1750 $\mathrm{J\,mol^{-1}}$ to compare with the experimental results. It can be seen from these figures that the agreement between experimental data and theoretical calculation is excellent.

Substituting Eq. (3) into Eq. (8), we have

$$\Delta S=\frac{3\alpha_0\beta_\infty}{8\gamma}\exp\left(-\frac{B}{d}\right), \tag{10}$$

so

$$\ln(\Delta S)=-\left(\frac{B}{d}\right)+\ln\left(\frac{3\alpha_0\beta_\infty}{8\gamma}\right). \tag{11}$$

This formula gives a linear relationship between $\ln(\Delta S)$ and $1/d$, with gradient $-B$. From the experimental values, the measured gradient is -80 nm.[2,15] Thus $B=80\,\mathrm{nm}$ for $PbTiO_3$.

C. Size effect on the crystal structure (c/a ratio)

According to the Devonshire[18] calculation, $(c/a-1)$ is proportional to P_s^2. Therefore, we have

$$\eta(d)\equiv\frac{c}{a}-1=KP_s^2(d), \tag{12}$$

where K is a constant.

Substituting Eq. (5) into Eq. (12), choosing the appropriate value for K, and putting $\eta(d=\infty)=0.0652$, which is the bulk value for $PbTiO_3$, we have

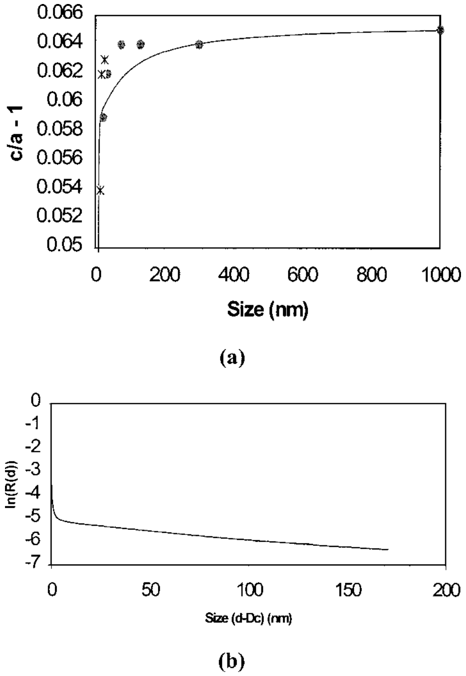

FIG. 4. (a) Size dependence of the c/a ratio. (b) Relationship between $\ln\{R(d)\}$ and $(d-D_c)$ In (a) ●, from Zhong *et al.* (Ref. 2); $*$ from Ishikawa *et al.* (Ref. 4).

$$\begin{aligned}R(d)&\equiv \eta(d=\infty)-\eta(d)\equiv\left(\frac{c}{a}\right)_{d=\infty}-\left(\frac{c}{a}\right)_{d}\\&=K[P_s^2(d=\infty)-P_s^2(d)].\end{aligned}\tag{13}$$

Figure 4(a) shows the size dependence of $\eta(d)$ for PbTiO$_3$ particles; the solid line is the theoretical calculation, and solid and open circles are experimental data measured by x-ray diffraction. $\ln\{R(d)\}$ versus reduced particle size $(d-D_c)$ is shown in Fig. 4(b). Clearly, this is a linear relationship when the particle size is larger than 25 nm. So the relationship between $R(d)$ and $(d-D_c)$ can be written approximately in the exponential form

$$R(d)\equiv\left(\frac{c}{a}\right)_{d=\infty}-\left(\frac{c}{a}\right)_{d}\approx K\exp[-C(d-D_c)],\tag{14}$$

where D_c is the critical particle size and C and K are constant. When d is equal to D_c, the particle changes to the paraelectric phase and $(c/a)_{d=D_c}=1$. Substituting into Eq. (14), we obtain

$$K=\left(\frac{c}{a}\right)_{\infty}-1.\tag{15}$$

Formula (13) can be rewritten as

$$\left(\frac{c}{a}\right)_{d}=\left(\frac{c}{a}\right)_{\infty}-\left[\left(\frac{c}{a}\right)_{\infty}-1\right]\exp[-C(d-D_c)].\tag{16}$$

This is the empirical formula obtained by Chattopadhyay *et al.* from experimental values of PbZrO$_3$ and PbTiO$_3$ particles.[5,6] This formula is a very good approximation for relatively larger particles. For example, it applies above 25 nm for PbTiO$_3$ fine particles very well.

D. Size effect on the dielectric property

From Eq. (1), the susceptibility below the Curie temperature $T_c(d)$ can be obtained as,

$$\begin{aligned}\chi_1(T,d)&=\left.\frac{\partial^2 A}{\partial D^2}\right|_{E=0}=\alpha(T,d)+3\beta(d)D^2+5\gamma D^4\\&=-4\alpha(T,d)+\frac{3\beta^2(d)}{\gamma}\left[1+\sqrt{1-\frac{4\alpha(T,d)\gamma}{\beta^2(d)}}\right].\end{aligned}\tag{17}$$

Above the Curie temperature, the susceptibility is

$$\chi_2(T,d)=\frac{1}{\alpha(T,d)}.\tag{18}$$

For ultrafine particles, it is assumed that the particle size d is distributed about an average size d_0 according to a Gaussian distribution function of the form

$$f(d)=f_0\exp\left[-\frac{(d-d_0)^2}{2\sigma^2}\right],\tag{19}$$

where σ is the standard deviation and f_0 is the normalization factor. Defining a deviation factor $\xi=\sigma/d_0$ to represent the spread of particle sizes, the effective susceptibility is then

$$\begin{aligned}&\chi_{\text{effect}}(T,d_0)\\&=\frac{\int_0^{d_c(T)}\chi_2(T,d)f(d)dd+\int_{d_c(T)}^{\infty}\chi_1(T,d)f(d)dd}{\int_0^{\infty}f(d)dd},\end{aligned}\tag{20}$$

where $d_c(T)$ is the critical size at temperature T. If the temperature is higher than T, all the particles having size less than $d_c(T)$ will be in the paraelectric phase.

In this model the real integration is taken from the critical size d_c to ∞ because the model is invalid when the crystal size is below d_c. The above equation becomes

$$\begin{aligned}&\chi_{\text{effect}}(T,d_0)\\&=\frac{\int_{d_c}^{d_c(T)}\chi_2(T,d)f(d)dd+\int_{d_c(T)}^{\infty}\chi_1(T,d)f(d)dd}{\int_{d_c}^{\infty}f(d)dd}.\end{aligned}\tag{21}$$

Figure 5 shows the susceptibility versus temperature for different particle sizes and deviation factors ξ. The dielectric peak decreases and moves to lower temperatures when the particle size decreases. Also, with a larger deviation factor ξ, the dielectric peak becomes smaller and diffuse, in agreement with the experimentally measured results for BaTiO$_3$, PbTiO$_3$ ferroelectric, and PbZrO$_3$ antiferroelectric particles.[1,5,6,20] Note that we do not try to explain the size effect on the dielectric constant measured at room temperature for BaTiO$_3$ (Ref. 21) and PbTiO$_3$ (Ref. 22) ultrafine particles by this theory. That behavior has been explained

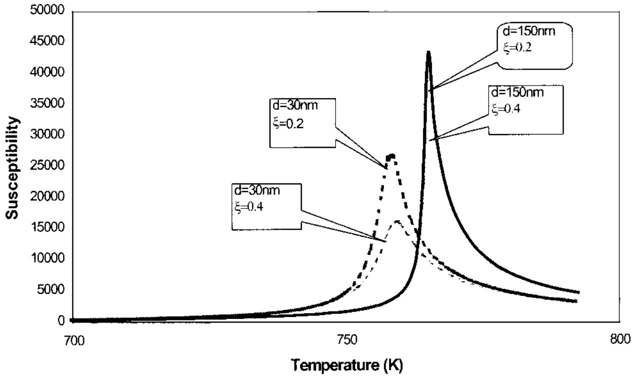

FIG. 5. Dielectric susceptibility of different particle sizes and deviation factors.

successfully by Shaikh *et al.*[21] by taking the effects of strain and domain walls into consideration.

E. Validity of our model

The inverse relationship between the LGD coefficient $\alpha(d)$ and the particle size d makes the model invalid when the particle size is less than d_c. The inverse relationship forces the $\alpha(d)$ to diverge at d_s and gives invalid results below d_c. Therefore, our model cannot be used when the particle size is less than d_c. This problem stems from the simple assumption used for $\alpha(d)$. The relationship was obtained from experimental empirical formulas and it is a good approximation for relatively lager particles. When the particle size becomes very small, the inverse relationship is invalid and another kind of formula should be proposed to discuss the physical properties of smaller particles. At present, there are not enough experimental data to realize an approximate formula for $\alpha(d)$ of particle size near and below d_c. This model was based on the Landau general phase transition theory. It may be valid for all ferroelectric and antiferroelectric particles with first-order paraelectric-ferroelectric phase transitions.

IV. RELATIONSHIP WITH THE MODEL OF ZHONG *et al.*

In the original mode of Zhong *et al.*, only surface effects and nonequilibrium effects were taking into consideration in the free energy formula. They assumed that the LGD coefficients were size independent. The model introduced here takes size effects on the LGD coefficients into consideration. Furthermore, surface effects and nonequilibrium terms are considered and reintroduced into the size dependence of the LGD coefficients. Thus the coefficients should be the effective coefficients of the particle. By this modification, the thermal properties of ferroelectric particles can be explained successfully. Another advantage of this model is the simpler free energy expression. It can be solved easily, and the physical properties can be discussed analytically.

V. SUMMARY

An improved phenomenological theory is proposed by taking the size effects on the LGD coefficients into account. By assuming the size dependence of the LGD coefficients α and β, one can successfully explain the size effects on physical properties of $PbTiO_3$-type ferroelectric particles, including the thermal property, c/a ratio, dielectric property, and Curie temperature. Our model also predicts a size-driven phase transition for which the ferroelectricity disappears when the particle size reaches a critical particle size.

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