

Is Barrett Equation Universally Applicable for Explaining Dielectric Constant of Ferroelectrics and Ferroelectric Thin Films?

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Abstract

Slater's formula for perovskite ferroelectrics was modified by Barrett to include the quantum effect. Dielectric constant vs temperature (ϵ' vs. T) data for Strontium titanate (ST) and Potassium tantalate (KT) in single crystals and ceramics fitted well, while the data (ϵ' vs. T) for Barium titanate (BT) in single crystals and ceramics did not fit at all to Barrett's equation. That is, ferroelectrics like ST, which show only Curie-Weiss temperature but does not show a ferroelectric transition, obey Barrett's equation. The Curie-Weiss law fitted the data of BT well. That KT a cubic and consequently a paraelectric down to 13 K obeys Barrett's equation is intriguing. ϵ' vs T values of Barium strontium titanate ($\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$), thin films could be fitted to the Curie-Weiss law, thus eliminating the existence of quantum effect in thin films.

Keywords: Barrett's equation; Curie-Weiss law; Perovskites; Ferroelectric materials; Barium titanate; Strontium titanate; Potassium tantalate; Barium strontium titanate.

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1. Introduction

Slater's classical theory [1] for ferroelectric perovskites such as barium titanate (BaTiO_3 , BT) was to explain the behavior of dielectric constants with temperature. Barrett [2] introduced a correction to Slater's theory by treating the system quantum mechanically. Barrett's expression for the potential energy of Titanium ion in an electric field is given by

$$\phi = a(x^2 + y^2 + z^2) + [b_1(x^4 + y^4 + z^4) + 2b_2(x^2y^2 + x^2z^2 + y^2z^2)] - q(xE_x + yE_y + zE_z) \quad (1)$$

which differs from Slater's equation in the last term involving $-q(xE_x + yE_y + zE_z)$. Barrett first solves for the terms independent of b 's and then treats the terms involving b_1 and b_2 together as a perturbation. Thus, if ϕ_1 is the potential energy of the Hamiltonian operator, the problem, according to Barrett, is that of a simple harmonic oscillator in an electric field [2]. Following long calculations, Barrett expressed the dielectric constant (ϵ') as,

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$$\varepsilon' = \frac{C}{\left(\frac{T_1}{2}\right) \coth\left(\frac{T_1}{2T}\right) - T_c} \quad (2)$$

where C is the Curie constant, T_c is the Curie temperature, $T_1 = hv/k$. T_1 is the temperature that is above T_c , and further below T_1 , the quantum effect will be observed, while above T_1 , the classical Curie-Weiss law can well explain the behavior of variation of ε' with temperature [2,3]. In other words, the quantum effect is important in ferroelectric perovskites at low temperatures, according to Barrett.

Following Barrett's paper [2], a number of workers published papers [3-6] on experimental aspects of perovskite in ceramics and in crystals at different temperatures, even as low as 0.3 K [4,5]. Besides, Barrett's theory was reformulated in sophisticated ways [6]. But, none raised the simple question, "If quantum effect exists in ferroelectric perovskites, what is the indicator or marker in an experiment such as ε' vs. T ?" The other question is "Does quantum effect exist in all perovskites, which indeed are ferroelectric?"

We thought about whether perovskite thin films, such as SrTiO_3 (ST), $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST), BaTiO_3 (BT), also exhibit quantum effects. In what follows, we also report our ε' vs. T measurements and check the validity of Barrett's equation for these systems.

2. Results and Discussion

2.1. Applicability of Barrett's equation in single crystal and ceramics of some perovskites

BaTiO_3 (BT), SrTiO_3 (ST), and KTaO_3 (KT) are all perovskites with the same perovskite structure. First, none of them belong to the same space lattice. Secondly, they undergo crystal transitions at different temperatures. We intend to include the structural results here. Barium titanate BaTiO_3 (BT) undergoes transitions: Rhombohedral $\xrightarrow{223 \text{ K}}$ Orthorhombic $\xrightarrow{273 \text{ K}}$ Tetragonal $\xrightarrow{393 \text{ K}}$ Cubic [7-9]. Strontium titanate SrTiO_3 (ST) undergoes a structural phase change from cubic to tetragonal phase at 106 K [10-12]. Potassium tantalate KTaO_3 (KT) is cubic above 13 K [5,13].

Barium titanate is a good example of perovskite that exhibits perfect ferroelectric transition at 393 K. Barrett used the values of $T_1=410n$ K, where $n \geq 1$ in Slater's result [2] to predict a value of 410 K for T_1 where $T_c = 390$ K. He did not compare his Eq. (2) with any experimental values of ε' vs. T of BT. Using the values of ε' vs. T of BT reported by Cochran [14], Bunting *et al.* [15] in single crystal and ceramic, attempts to fit the experimental data to Eq. (2), using T_1 and T_c reported by Barrett [2], did not succeed. Results are given in Fig. 1. Curve (a) and curve (b) represent the experimental results of Cochran [14] and Bunting *et al.* [15], respectively, while curve (c) shows the plot of Eq. (2) with $T_1= 410\text{K}$ and $T_c = 393$ K. Besides, we tried to fit the data with different values of T_1 but $T_c = 393$ K to eq. (2). But it did not succeed.

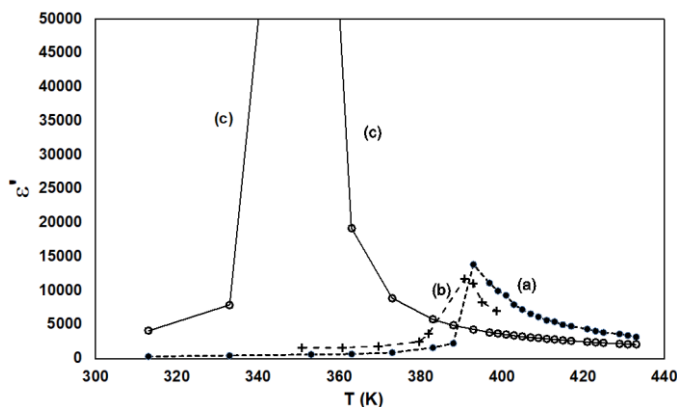


Fig. 1. Plot of Barrett eq. (2) for BaTiO₃ using T₁ = 410 K, T_c = 393 K shown in curve (c). Curve (a) and curve (b) show the experimental data of Cochran [14] and Bunting *et al.* [15] for BaTiO₃ single crystal and ceramic, respectively.

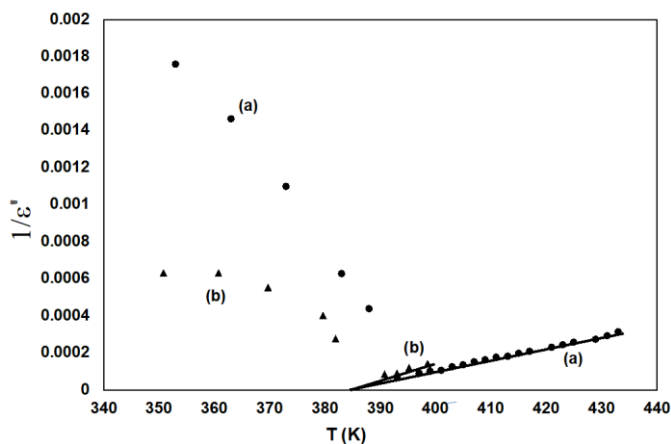


Fig. 2. Curie-Weiss law fitting to 1/ε' vs. T data of Cochran [14] (curve (a)) for single crystal BT, curve (b) for ceramic BT for Bunting *et al.* [15].

Next, it was tried to fit the experimental results of 1/ε' vs. T of Cochran [14] and Bunting *et al.* [15] to Curie-Weiss law. Results are given in Fig. 2. A good fit was observed for temperatures above 393 K with the Curie-Weiss temperature of 382 K.

Strontium titanate (ST) is a perovskite like BaTiO₃, where Ba²⁺ is replaced by Sr²⁺ ions only. However, it does not exhibit a ferroelectric transition at the structural crystal transition temperature of 106 K [10] and, in reality, at any temperature down to 0.3 K [4,5]. A number of workers [4-6] have studied ε' vs. T with samples of ST as ceramics and single crystals. Here, T_c or Curie-Weiss temperature is calculated from 1/ε' vs. T plot. Different authors have used different combinations of T_c and T₁ values to fit Barrett's Eq. (2). Barrett used T_c = 35 K and T₁ = 60 K for interpreting Hulm's results [11]. In comparison, he required T₁ = 100 K to interpret Youngblood's results [16] on ST. Weaver

[4] used $T_c = 45$ K and $T_1 = 100$ K, while Muller *et al.* [5] used $T_c = 38$ K and $T_1 = 84$ K. Recently, Yuan [6] used two sets of parameters of $T_c = 35.5$ K, $T_1 = 77.8$ K and $T_c = 35.5$ K, $T_1 = 80$ K to fit the experimental ϵ' vs. T data for ST of Salje *et al.* [17]. The variation in T_c and T_1 values, required to fit Eq. (2), of samples of ST prepared by different workers can be associated with sample preparation. Both Weaver and Muller observed saturation in the value of the dielectric constant at very low temperatures of 10 K and lower. Fig. 3 includes ϵ' vs. T curves of Weaver [3] and Muller [4,5] (all represented by dashed lines) along with the theoretical fitting curves using their respective values of T_1 and T_c . All the experimental data show a saturation in the value of dielectric constants at temperatures lower than 20 K or 10 K. Reasonably good fits to Barrett's equation were obtained for the ϵ' vs. T values of ST samples.

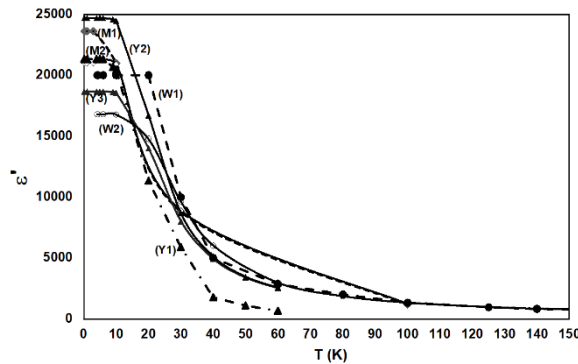


Fig. 3. Plot of Barrett eq. (2) for SrTiO₃ using different values of T_1 and T_c . Curves (W1), (M1), (Y1) represent the experimental data of ϵ' vs. T data of Weaver (W) [3], Muller *et al.* (M) [4,5], Yuan *et al.* (Y) [6] for ST single crystals. Curves (W2), (M2), (Y2), and (Y3) represent the plot of Barrett's equation using their values of T_1 and T_c .

Next, the applicability of Curie-Weiss law was also investigated for these samples of ST. $1/\epsilon'$ vs. T curves given in Fig. 4 show that the Curie-Weiss law is valid above 50 K.

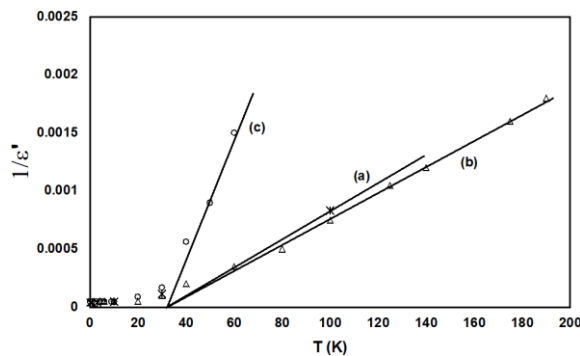


Fig. 4. Plot of $1/\epsilon'$ vs. T for verifying Curie-Weiss law for SrTiO₃ single crystal. Symbols represent the experimental points, and the straight lines fit the Curie-Weiss law. Curve (a) is for Muller's data, curve (b) is for Weaver's data, and curve (c) is for Yuan's data.

Potassium tantalate, KTaO_3 (KT), is also a perovskite. Initially, it was considered to be ferroelectric, which was later shown to be cubic above 13 K [4,16,18]. Interestingly, Barrett used ϵ' vs. T values of Hulm *et al.* [13], which fitted his equation very well. Using the data reported by Fujishita *et al.* [19] for single crystal KT, we tried to check the validity of Barrett's equation. The results are reported in Fig. 5. For $T_1=55$ K and $T_c=14$ K, a good fit to Barrett's equation was observed. Plot of $1/\epsilon'$ vs. T for KT given in Fig. 6 shows the validity of Curie-Weiss law above 60 K.

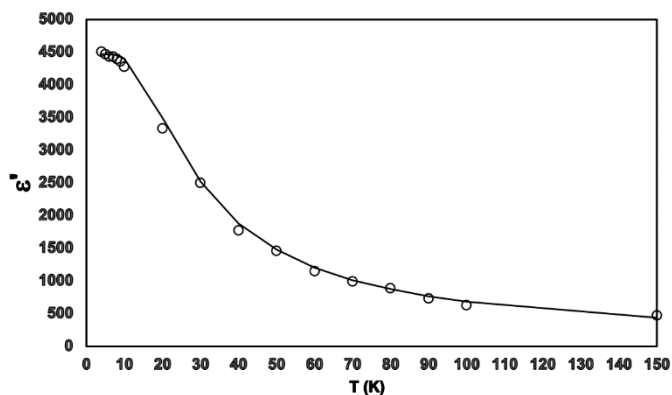


Fig. 5. Fitting of Barrett eq. (2) to ϵ' vs. T data of Fujishita *et al.* [18] single crystal KT using $T_1 = 55$ K, $T_c = 14$ K. Empty circles show the experimental data [18], and solid lines represent the fitting of equation (2).

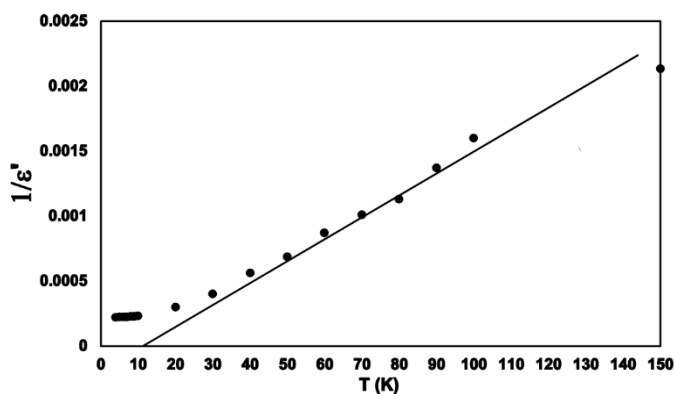


Fig. 6. Plot of $1/\epsilon'$ vs. T for verifying Curie-Weiss law for KTaO_3 single crystal. Symbols represent the experimental points, and the straight line represents the fit to Curie-Weiss law for the data of Fujishita *et al.* [19].

2.2. Applicability of Barret's formula in thin films

Solid solutions of Barium strontium titanate ($\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$) (BST) show perovskite structure with the transition temperature varying between that of BaTiO_3 and SrTiO_3 depending on the composition (x). Dielectric properties of various compositions of sol-gel deposited Barium strontium titanate films were reported in our earlier paper [21]. A variation of T_c was observed from 93 K for $x = 0.1$ to 398 K for $x = 1.0$ for our sol-gel thin films of $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ [21]. The observed ferroelectric transition temperatures were close to those reported for single crystals and ceramics [15,22]. Ferroelectric transition temperature could not be detected in strontium titanate ($x = 0.0$) thin films down to liquid nitrogen temperature [21].

Here, it is tried to check whether Barrett's Eq. (2) is valid in thin films or whether the Curie-Weiss law is sufficient to explain the behavior of ferroelectric thin films.

As reported in our earlier paper for thin films, the dependence of dielectric constant with temperature (ϵ' vs. T) can be given by a modified equation (3) [21],

$$\frac{1}{\epsilon'} = \frac{1}{\epsilon'_{(peak)}} + \frac{T-T_c}{C} \quad (3)$$

where, C is the Curie constant, and T_c is the transition temperature.

Using Eq. (3), Barrett's Eq. (2) will be modified to,

$$\frac{1}{\epsilon'} = \frac{1}{\epsilon'_{peak}} + \frac{\left(\frac{T_1}{2}\right) \coth\left(\frac{T_1}{2T}\right) - T_c}{C} \quad (4)$$

where ϵ' is the measured dielectric constant, ϵ'_{peak} is the peak value of the dielectric constant, C is the Curie constant, T_c is the transition temperature, and T_1 is the temperature below which quantum effect is valid as suggested by Barrett.

First, the applicability of Barrett's equation is checked for the ST films. Fig. 7 shows the fitting of Eq. (4) with our experimental data of ϵ' vs. T of thin films of Strontium titanate, where the Curie constant (C) for $x=0.0$ is 8.54×10^4 K [21]. It was observed that none of the combinations of T_c and T_1 reported for crystals of ST fitted the experimental data of ST in thin films for the entire temperature range studied (88 K to 333 K). No reasonable value of T_1 could be obtained to fit the experimental data of ϵ' vs. T for ST.

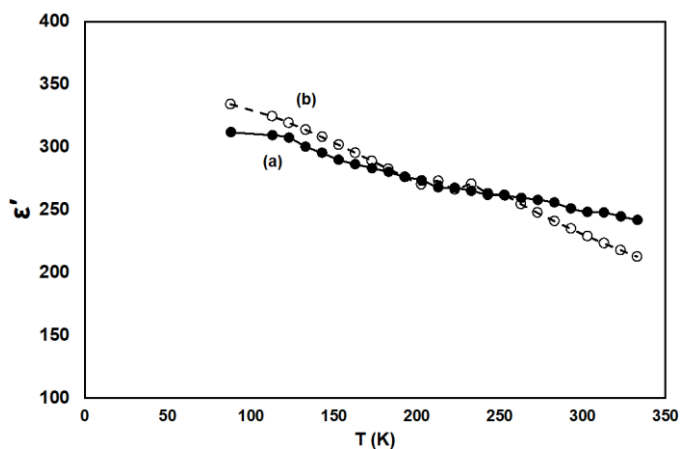


Fig. 7. Fitting of Barrett's eq. (4) for Strontium titanate thin films. Curve (a) shows our experimental data, and curve (b) shows the possible fitting to the experimental data using different values of T_1 .

Attempt is also made to fit our experimental results of ϵ' vs. T of Barium titanate (BT) thin films to Barrett's equation.

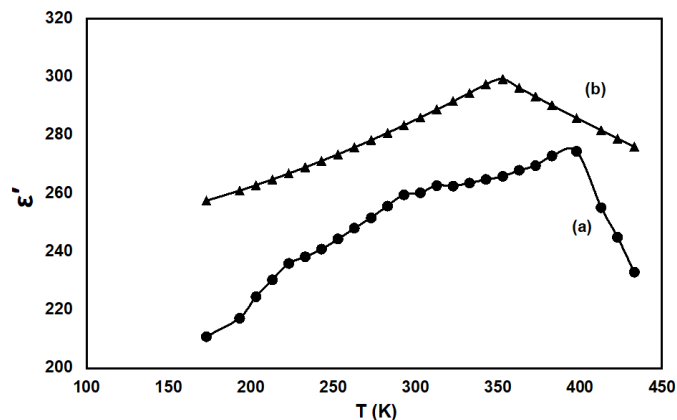


Fig. 8. Fitting of Barrett's eq. (4) for Barium Titanate thin films using T_c and T_1 values of Barrett [2] (curve (b)). Experimental values are shown by curve (a).

The value of C is 2.6×10^5 K [21]. Results are given in Fig. 8, where curve (a) shows our experimental result and curve (b) shows the plot of ϵ'' vs. T plot of Eq. (4) using $T_1 = 410$ K as suggested by Barrett for BT in ceramics. The experimental data could not be fitted with Eq. (4) even when we take other values of T_1 .

Next, T_1 was tried to measure for other compositions of BST by trying to fit Eq. (4) with the experimental results, but no reasonable value of T_1 could be found for any composition of BST. This shows that for thin films of $Ba_xSr_{1-x}TiO_3$, with $x = 0.0, \dots, 1.0$, Barrett's equation, which takes into account the quantum effect, is not required.

In the absence of quantum effect, the variation of measured dielectric constant with temperature will be given by Curie-Weiss law [1]. Fig. 9 includes the results of $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ for compositions with $x = 0.4$ and 0.0 in thin films. A good fitting was observed for the entire paraelectric phase for all the compositions of BST, exhibiting that the Curie-Weiss law is enough to explain the behavior of ϵ' vs. T for thin films. Since no reasonable value of T_1 was obtained for thin films, we can consider that the quantum effect suggested by Barrett may not be important in thin films. Much more detailed studies may be required to find why the quantum effect is either not observed or is not required in thin films of BaSrTiO_3 . Skormets *et al.* [20] reported ϵ' vs. T for sol-gel thin films of KT. The transition was observed at 15 K, and the data can be fitted to Curie-Weiss law above 80 K. There exist a large number of results showing the applicability of Curie-Weiss law in ferroelectric materials in thin films [21,23-27].

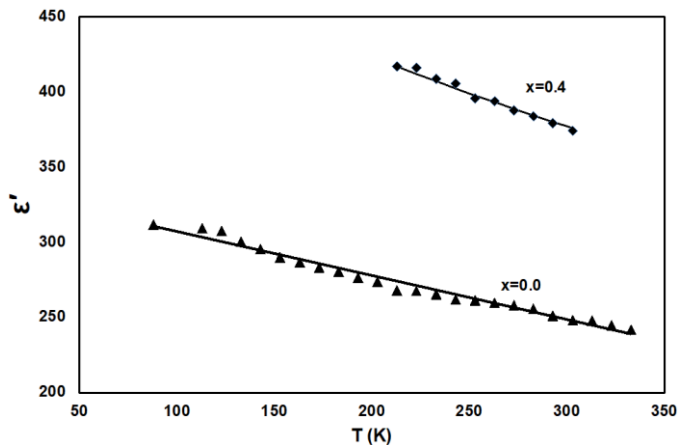


Fig. 9. Verification of Curie-Weiss law for two compositions $x=0.0$ and $x=0.4$ for $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ thin films.

3. Conclusion

The perovskite BaTiO_3 , which displays a sharp ferroelectric transition at 393 K, does not exhibit any quantum effect in ϵ' vs. T values. It obeys a Curie-Weiss law. Calcium titanate also exhibits a sharp ferroelectric transition at a high temperature of 1636 K. It is the least studied perovskite. We do not find any report that it exhibits any quantum effect. The other perovskite in the series, SrTiO_3 , which ought to show a ferroelectric transition at 106 K [10], does not exhibit any such transition at 106 K or down to 0.3 K [4,5]. The values of the dielectric constant as a function of temperature below 150 K are fitted with Barrett's Eq. (2). Hence, SrTiO_3 exhibits a quantum effect. It can be inferred that a perovskite that exhibits only Curie-Weiss temperature and does not exhibit any ferroelectric transition may exhibit a quantum effect.

Now, the ionic radii of Ba^{2+} , Sr^{2+} and Ca^{2+} are, respectively, 1.43 Å, 1.27 Å, and 1.06 Å. It is difficult to accept why ST does not exhibit ferroelectric transition at a higher

temperature while BaTiO₃ and CaTiO₃ do exhibit. It is desired that a detailed X-ray structural study rather than a simple space group determination is required for ST. That will reveal why the long-range ordering that is essential for a sharp ferroelectric transition does not exist or operate in SrTiO₃. We hope research may be directed in ferroelectrics to get direct experimental evidence of quantum effect in a customized experiment.

Potassium tantalate, KTaO₃, is cubic down to 13 K and does not exhibit any ferroelectric transition. Yet, Barrett's Eq. (2) fits the experimental data. This raises a serious question. Slater's classical theory was for perovskite ferroelectric, BaTiO₃, which shows ferroelectric transition. Barrett introduced the quantum effect into this theory. But a paraelectric like KTaO₃ exhibits a quantum effect since the data fits Eq. (2). It is rather intriguing.

Barrett's formula for perovskite ferroelectrics was investigated for sol-gel deposited thin films of various compositions of Barium strontium titanate (Ba_xSr_{1-x}TiO₃) where x varied from 0.0, 0.1, 0.2, ... 1.0. A good fit was not observed for reasonable values of T₁ for different compositions of BST thin films. Our result shows that for thin films, the Curie-Weiss law is sufficient to explain the behavior of dielectric constant with temperature in the paraelectric phase. The quantum effect is not evident in thin films at all.

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