

ON THE DIELECTRIC CURIE-WEISS LAW AND DIFFUSE PHASE TRANSITION IN
FERROELECTRICS

G.H. Jonker
Department of Electrical Engineering
Twente University of Technology
Enschede, The Netherlands

Dedicated to Professor Albrecht Rabenau on the occasion of his 60th birthday

(Received January 17, 1983; Communicated by R. A. Huggins)

ABSTRACT

A simple derivation of parabolic $1/\epsilon_r$ -T curves is obtained by reconsidering the origin of the dielectric Curie-Weiss law. The only assumption needed is the introduction of a non-linear temperature dependence of the macroscopic dielectric polarization in the macroscopic Clausius-Mossotti equation.

Introduction

Barium titanate, the first oxidic ferroelectric, free of permanent dipoles, is the standard example of compounds with a first order ferroelectric phase transition. The first characteristic feature, announcing the ferroelectricity, is the strong variation of the dielectric constant ϵ_r with temperature in the high temperature paraelectric state as

$$\epsilon_r = \frac{C}{T-T_0} \quad (1)$$

analogous to the magnetic Curie-Weiss law. The second and most important property is the structural instability at or near the temperature T_0 , which leads to a new, spontaneously polarized structure of the ionic crystal lattice.

A fairly large group of compounds show qualitatively analogous properties, but with varying values of the parameters C and T_0 . Moreover solid solutions of such compounds show a gradual shift of these parameters.

A few groups with rather complicated compositions, however, show rather strong deviations from these characteristic aspects.

In one group of such compounds it has been found that these deviations are related to a local variation in order or disorder, as e.g. in $Pb_2 Sc Nb O_6$ (1). Such compounds are excluded in this paper.

Another group, that receives our special attention, consists of modifications of $Pb(Zr, Ti)O_3$ (PZT) solid solutions with partial replacement of Pb by La, Sr or Ba. Especially the modifications with La have attracted much attention as they can be prepared in ceramic form to such a high quality, that they are optically transparent and show interesting and technically important electro-optical properties (2).

These materials are characterized by the facts that the ϵ_r -T curves strongly deviate from the Curie-Weiss law, that the originally sharp peak of ϵ_r at the transition temperature T_c continuously broadens with increasing degree of substitution and that the maximum value of ϵ_r , which may be as high as 15000 - 25000, decreases to much lower values, below 5000. An example of such ϵ_r -T curves is shown in figure 1. Also, the tendency to spontaneous

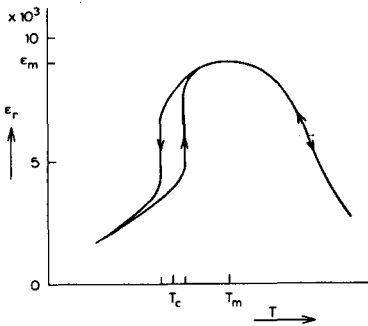


FIG. 1: Schematic example of PLZT ferroelectric transitions with $T_c < T_m$.

polarization disappears, but a remarkable new phenomenon is, that in certain intermediate compositions the ferroelectric transition can be induced by an electric field. A number of theories about these remarkable effects have been proposed, but none of them have been completely satisfactory. The main theories are based either on compositional fluctuations or on polar fluctuations around the Curie temperature.

In this paper we shall attempt a different approach to these problems by making a new study of the origin of the ferroelectric transition in a general way.

The dielectric Curie-Weiss law

Our treatment is based on the derivation of the original dielectric Curie-Weiss law. In the context of this paper the macroscopic, phenomenological theory is used which can be applied to crystals of cubic symmetry as well as to polycrystalline materials (3). For the physical background of our results, however, the study of the microscopic properties is of fundamental interest.

The starting point is the dielectric Clausius-Mossotti equation applied to a small spherical part inside a large sample, with a volume v and a total polarizability α .

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{1}{3\epsilon_0} \frac{\alpha}{v} \tag{2}$$

(m k s units)

Then, starting at a temperature T_s and the values ϵ_s and $(\frac{\alpha}{v})_s$, and assuming a linear temperature dependence of both α and v , equation (2) can be written as:

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{1}{3\epsilon_0} \left(\frac{\alpha}{v}\right)_s \left(1 - 3a (T - T_s)\right) = \frac{\epsilon_s - 1}{\epsilon_s + 2} \left(1 - 3a (T - T_s)\right) \tag{3}$$

$$- 3a = - \frac{1}{v} \left(\frac{\delta v}{\delta T}\right)_p + \frac{1}{\alpha} \left(\frac{\delta \alpha}{\delta v}\right)_T \frac{dv}{dT} + \frac{1}{\alpha} \left(\frac{\delta \alpha}{\delta T}\right)_v \tag{4}$$

$$\equiv C_1 + C_2 + C_3$$

According to Havinga (3) and to Bosman and Havinga (4) the three contributions C_1 , C_2 and C_3 are of the same order of magnitude, but for materials with high ϵ_r values C_1 and C_2 are negative and C_3 positive. This explains that in the literature either C_1 (experimentally (5)) or C_3 (theoretically (6)) has been considered as the most important contribution.

For high values of ϵ_r equation (3) can be transformed into:

$$\frac{1}{\epsilon_r} = \frac{1}{\epsilon_s} + a(T-T_s) \tag{5}$$

and to:

$$\frac{1}{\epsilon_r} = a(T-T_o) \quad \text{or} \quad \epsilon_r = \frac{C}{T-T_o} \tag{6}$$

with $T_o = T_s - \frac{1}{a\epsilon_s}$ and $C = \frac{1}{a}$

Equation (6) is called the dielectric Curie-Weiss law for dipole-free compounds, but, if compared with the original magnetic law of this name, with a totally different meaning for C and T_o . It is, therefore, questionable whether this simple rule should be called a "law"!

Extension of the Curie-Weiss law

Normally, a series of solid solutions of two perovskite compounds, e.g. $BaTiO_3$ - $SrTiO_3$, shows a gradual shift of the Curie temperature T_o and a slight variation of the Curie constant C. It is, therefore rather a shock that in series of modified PZT solid solutions strong deviations gradually develop. As qualitatively similar deviations occur in La, Sr or Ba modified PZT it is not correct to consider lattice vacancies accompanying La as the origin of these deviations (7).

In view of the gradual appearance of the deviating behaviour we need a theory covering the whole range of compositions. In spite of the rather complicated composition there is no doubt about the validity of at least the macroscopic Clausius-Mossotti equation (2), and also no doubt about the fact that α/v will show a certain temperature dependance. In the derivation of the Curie-Weiss law this temperature dependance had been described by a first order term only (equation (3)) which fortunately holds quite well for many of the first detected ferroelectrics. Phenomenologically, however, there is no objection to try a further expansion of this first order approach for more complicated materials with locally varying asymmetric surroundings of the ions:

$$\frac{\epsilon_r^{-1}}{\epsilon_r+2} = \frac{1}{3\epsilon_o} \left(\frac{\alpha}{v}\right)_s \left(1 - 3a(T-T_s) - 3b(T-T_s)^2 + \dots\right) \tag{7}$$

It is quite elucidating to study in the first place the effect of the addition of the quadratic term in equation (7). This equation can then, again for large values of ϵ_r and in a comparable way as equation (3) be transformed to:

$$\frac{1}{\epsilon_r+2} = \frac{1}{\epsilon_s+2} + \frac{\epsilon_s^{-1}}{\epsilon_s+2} \left(a(T-T_s) + b(T-T_s)^2\right) \tag{8}$$

and, neglecting the 2's and $\frac{\epsilon_s^{-1}}{\epsilon_s+2}$ (which is slightly inexact) to:

$$\frac{1}{\epsilon_r} = \frac{1}{\epsilon_m} + b(T-T_m)^2 \tag{9}$$

with $\frac{1}{\epsilon_m} = \frac{1}{\epsilon_s} - \frac{a^2}{4b}$ and $T_m = T_s - \frac{a}{2b}$

For positive values of b a minimum of $1/\epsilon_m$ occurs at a temperature T_m . Equation (9) corresponds to the experimental quadratic description found originally by Smolensky (8) and by Kirillov and Isupov (9) for $Pb_3 Mg Nb_2 O_9$ and solid solutions and later by Wolters and Burggraaf (10) for series of modified PZT materials.

In equation (9) the leading role of the coefficient a has disappeared, but can be retraced as the temperature coefficient $a = 2b (T_s - T_m)$ at the starting temperature T_s .

An example of the influence of the quadratic term is shown in figure 2.

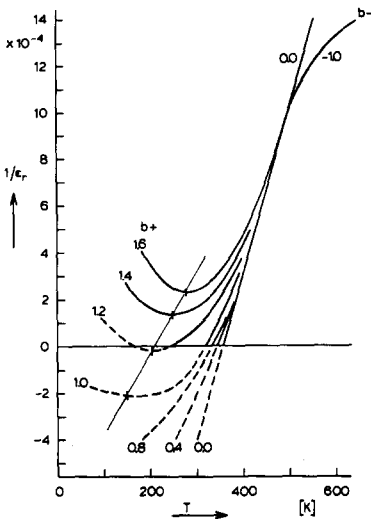


FIG. 2: Examples of parabolic $1/\epsilon_r$ - T curves with $a=0.7 \times 10^{-5}$ K and varying b values (in $10^{-8} K^{-2}$).

The group of curves starts from a normal ferroelectric with $\epsilon_s=1000$ at $T=500$ K and with $a=0.7 \times 10^{-5} K^{-1}$ and $b=0$, which gives $T_O=357$ K. Then gradually the value of b is increased from 0 to $1.6 \times 10^{-8} K^{-2}$. The sign of $1/\epsilon_m$ changes from negative to positive at a point where $a^2/4b = 1/\epsilon_s$, thus, in this case, for $b=1.23 \times 10^{-8} K^{-2}$.

This first result is quite promising, as many shapes of experimental $1/\epsilon_r$ - T curves can be recognized. All kinds of variations, shapes and shifts in temperature, can be obtained by varying ϵ_s , T_s , a and b . In practice, however, ϵ_m and T_m can be read immediately from the measured $1/\epsilon_m$ - T curves and b is calculated from the shape of these curves.

For the sake of completeness a curve with a negative b value is shown in figure 2. Examples of this type are not known.

It is clear that examples with very low b values are often not recognized, as such small deviations often occur due to a non-ideal sample preparation. Therefore, a precise analysis of experimental curves is only worthwhile if they cover a long temperature range and are measure on high quality materials.

Examples

Though many examples of diffuse phase transition have been described in literature e.g. by Smolensky (8) and by Haertling and Land (2), it is not easy to transform these measurements accurately into $1/\epsilon_r$ - T curves. Only in a few cases are enough details given. One such example is the work of Wolters and Burggraaf (10) on PLZT x/55/45, who also give the parameters b and T_m of the parabolic curves. These are not purely symmetric, but as a demonstration the original ϵ_r - T curves and simulated $1/\epsilon_r$ - T curves are shown in figure 3 and 4. One mean value of $1.0 \times 10^{-8} K^{-2}$ has been chosen for b . These curves give the impression that measurements on samples with lower x can also be simulated by quadratic curves, but with extrapolated negative values of $1/\epsilon_m$.

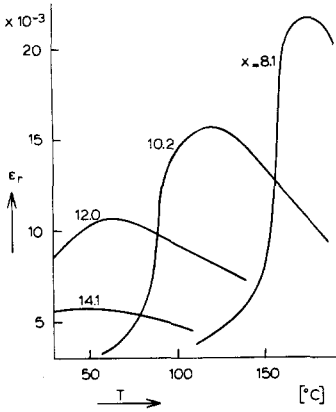


FIG. 3: ϵ_r -T curves of PLZT x/55/45 after (10).

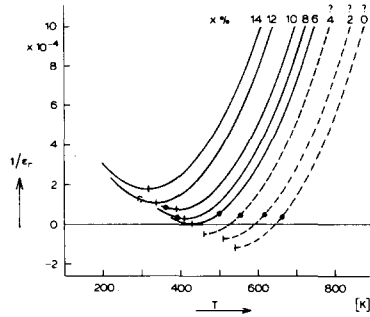


FIG. 4: Simulated $1/\epsilon_r$ -T curves of PLZT x/55/45 calculated from (10) with $b=10^{-8} \text{ K}^{-2}$ transition above T_m . 000 transition below T_m .

The second example is taken from the work of Stenger and Burggraaf (11) on the system PLZT x/30/70. These authors point out the fact that the temperatures T_0 , found by extrapolating the straight parts of their $1/\epsilon_r$ -T curves are much higher than the real transition temperatures. It could possibly be that these "straight" parts represent just a best fit to the expected Curie-Weiss law, but in reality form a part of the parabolic curves. In this case the measurements allow a simulation, again by using a value $b=1.0 \times 10^{-8} \text{ K}^{-2}$ (figure 5).

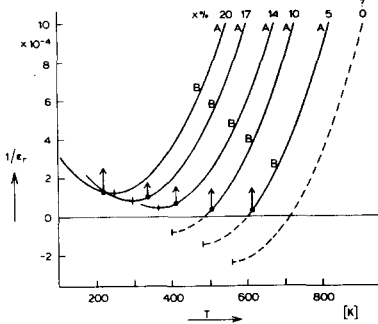


FIG. 5: Simulated $1/\epsilon_r$ -T curves of PLZT x/30/70 after (11), where the parts AB are considered to be linear. \uparrow Spontaneous transition points.

Thermodynamic considerations

In this section the consequences of the quadratic $1/\epsilon_r$ -T equation will be tested, by comparing the experimental features of the materials with properties that can be derived from the phenomenological thermodynamic approach of Devonshire.

The starting point for this approach is the free enthalpy function

$$G = G_0 + G(P) \text{ with}$$

$$G(P) = \frac{1}{2} \alpha P^2 + \frac{1}{4} \gamma P^4 + \frac{1}{6} \delta P^6 \quad (10)$$

It is clear that here α represents the $1/\epsilon_r$ function in the non-polar state $P=0$. The parameters γ and δ can be used to adapt the G -function to the experiments, but have no known physical meaning. As in our case the ferroelectric transition occurs at positive values of α a negative value of γ and a positive value of δ must be assumed. This approach is described in detail in textbooks on ferroelectricity, e.g. (12). It can easily be established that the various features derived from (10) have general validity if expressed in α , γ and δ , and that any function α can be filled in afterwards. In the neighbourhood of the Curie temperature the $G(P)$ functions show for a first order transition 5 extreme values (maxima and minima), gradually reducing to three extreme values at lower and to one minimum value only at higher temperatures (see figure 6).

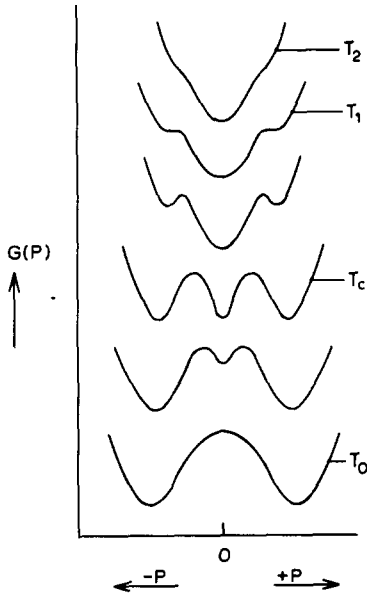


FIG. 6: $G(P)$ - P curves at various temperatures after (12).

this region, T_2 is characterized by:

$$\alpha = \frac{9}{20} \frac{\gamma^2}{\delta} \quad (13)$$

The combination of the eqs. (11), (12) and (13) with eq. (9) should lead to the set of characteristic temperatures T_0 - T_2 . Experimentally these temperatures occur above T_m if $1/\epsilon_m$ is negative, but below T_m if $1/\epsilon_m$ is positive. Further, of course, these temperatures should appear in the correct order. This proves to be impossible for temperature independent values of γ . It is demonstrated in figs. 7a-7c that only temperature dependent values of γ^2/δ lead to correct results, just as in the case of BaTiO_3 .

The Curie point T_C is defined as the temperature of equilibrium between the poled and the unpoled state (3 equal minima). For this situation holds:

$$\alpha = \frac{3}{16} \frac{\gamma^2}{\delta} \quad (11)$$

The thermal hysteresis of the transition is characterized by a temperature $< T_C$ on cooling and a temperature $> T_C$ on heating, where the transition occurs spontaneously, or, in other words, where the energy barriers have become low enough to be overcome by thermal motion. The lowest possible value for the lower one is the temperature T_0 where $\alpha=0$. At this point the central minimum of $G(P)$ disappears. The maximum possible value of the higher one is the temperature T_1 where the two minima at $+P$ and $-P$ disappear, characterized by:

$$\alpha = \frac{1}{4} \frac{\gamma^2}{\delta} \quad (12)$$

Further, there is a temperature region above T_1 where the ferroelectric transition can be induced reversibly by an electric field. The highest possible temperature of

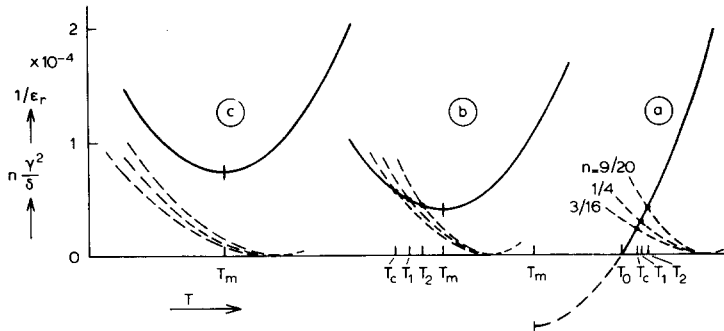


FIG. 7: Graphical construction of the temperatures T_0 , T_C , T_1 and T_2 from $1/\epsilon_r$ - T curves and $\alpha - \gamma^2/\delta$ relations. — $1/\epsilon_r$ versus T curves. ---- $\alpha = n\gamma^2/\delta$ versus T curves.

In figs. 7a-7c the gradual transition is shown from a "normal" behaviour if $1/\epsilon_m$ is negative (7a), to the disappearance of any ferroelectricity (7c), with in between the interesting case occurring if $1/\epsilon_m$ is slightly positive (7b). In this latter case we find two special features:

- a) There is no temperature T_0 where $\epsilon_r=0$ so that the central minimum of the G-P function never disappears. As a result it may occur that the lower temperature of the temperature hysteresis is missing, in other words, that the spontaneous polarization below T_C is absent. This is the case where the transition needs the help of an electric field, large enough to overcome the rest barrier between the non-poled and the poled state. On heating the normal transition at T_1 takes place.
- b) As the result of the flatness of the $1/\epsilon_r$ - T curve the distance between the temperature T_1 and T_2 will be quite large. This explains the fact that the temperature region of reversibly induced ferroelectricity (slim loop area) is much longer (20-30 K) than for normal ferroelectrics (5-8 K).

In the third example (figure 7c) the $1/\epsilon_m$ value is too high so that there is no crossing with the γ^2/δ curves. The only peculiar feature is the flat ϵ_r - T curve, but all ferroelectricity is absent. These materials may be of interest for capacitors only.

Discussion

A first impression is that the theory of the quadratic equation is strongly supported by the thermodynamic results of the preceding section. Unfortunately, however, these results are independent from the physical origin of the quadratic equation!

Therefore, the two main models leading to a quadratic $1/\epsilon$ - T relation have to be compared from a physical point of view:

- a) The compositional fluctuation model.
- b) The expansion of the Curie-Weiss law.

In our opinion there are no macroscopic objections against model b. This model will be strongly supported if more evidence can be obtained on the reality of simulated $1/\epsilon_r$ -curves having negative extrapolated $1/\epsilon_m$ values. It depends, however, on the further study of the microscopic background whether the proposed expansion is realistic, in the first place with regard to the sign of the parameter b.

In essence, also this model may depend on a kind of compositional fluctuation, but here per crystallographic unit, leading to a fluctuation in local polarizabilities and their temperature coefficients.

With respect to model a) two serious objections arise. This model is based on statistical composition fluctuations leading to fluctuations of the local Curie temperatures. In the complicated compositions of the PLZT materials this effect may contribute to a broadening of the Curie area and a quadratic $1/\epsilon_r$ -T law. However, the experimental equality of the values of b ($\approx 10^{-8} \text{ K}^{-2}$), e.g. in the series represented in figure 4, would demand an equal distribution of the Curie temperatures in all compositions. A difficulty then is the strong variation found for the $1/\epsilon_m$ values, which in this model should also be equal. Negative extrapolated $1/\epsilon_m$ values do not fit at all in model a).

A second objection is the fact that the real ferroelectric transition is not diffuse at all but sharp, and occurs far below T_m , which is in contrast to the idea that below T_m a greater part of microregions is already polarized. From this same point of view it is also not clear that in the presence of such a high concentration of poled microregions an electric field is sometimes needed to induce the macroscopic polarization.

From these considerations we arrive at the conclusion that our model with only one simple new assumption gives a worthwhile basis for the description and characterization of available materials and for the continuation of research in this field.

References

1. C.G.F. Stenger and A.J. Burggraaf, *Physica Status Solidi* 61, 275 (1980).
Physica Status Solidi 61, 653 (1980).
2. G.H. Haertling and C.E. Land, *J. Amer. Ceram. Soc.* 54, 1-11 (1971).
3. E.E. Havinga, *J. Phys. Chem. Solids* 18, 253-255 (1961).
4. A.J. Bosman and E.E. Havinga, *Phys. Rev.* 129, 1593-1600 (1963).
5. J.H. van Santen and G.H. Jonker, *Nature* 159, 333-334 (1947).
G.H. Jonker and J.H. van Santen, *Science* 109, 632-635 (1949).
6. J.C. Slater, *Phys. Rev.* 78, 748 (1950).
7. G.H. Jonker, R. Juárez, A.J. Burggraaf and C.G.F. Stenger, *Ferroelectrics* 24, 293-296 (1980).
8. G.A. Smolensky, *J. Phys. Soc. Japan, Suppl.* 28, 26 (1970).
9. V.V. Kirillov and V.A. Isupov, *Ferroelectrics* 5, 3 (1973).
10. M. Wolters and A.J. Burggraaf, *Mat. Res. Bull.* 10, 417-424 (1975).
11. C.G.F. Stenger and A.J. Burggraaf, *J. Phys. Chem. Solids* 41, 25-30 (1980).
12. E. Fatuzzo and W.J. Merz, "Ferroelectricity", North Holland Publishing Comp., Amsterdam 1967. John Wiley and Sons Inc., New York.

Note:

The author regrets that the work of dr. G. Schmidt escaped his attention:
G. Schmidt et al. *Phys. Stat. Sol. (a)* 63, 501(1981).