The Rhodes-Wohlfarth parameter as assessment of the displacive degree in ferroelectrics: The case of the Φ^4 model

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Abstract. The Rhodes-Wohlfarth parameter extended to ferroelectrics by Tokunaga [J. Phys. Soc. Jap. **57**, 4275 (1988)] is here analyzed within the Φ^4 model. It is shown that it can be directly related with the displacive degree of the transition as described by the ratio C/E_0, between the non-local coupling, C, driving the transition and the depth of the energy well, E_0, associated with the distorted structure. However, the Rhodes-Wohlfarth parameter becomes asymptotically constant as C/E_0 decreases, *i.e.* for systems closer to the order disorder limit. Under this viewpoint, the very limited range of values observed for this experimental parameter is explained and is shown that, in general, it can only assess quantitatively the character of the transition in rather displacive cases. The argument can be generalized to more complex systems, and when applied to well known materials, a rough estimation of the displacive degree and the relevant microscopic energetic parameters in rather displacive ferroelectrics is possible.

PACS. 64.70.Kb Solid-solid transitions – 64.90.+b Other topics in equations of state, phase equilibria, and phase transitions dynamics (restricted to new topics in section 64)

1 Introduction

Recently, the so-called Rhodes-Wohlfarth parameter, originally defined for ferromagnets, was extended by Tokunaga [1] into the field of ferroelectrics. This factor is generalized as:

$$R = \frac{1}{P_s}\sqrt{\frac{nk_B C_{c-w}}{4\pi}} \qquad (1)$$

where P_s is the saturated spontaneous polarization, C_{c-w} is the observed Curie-Weiss constant, n is the density of dipolar units and k_B is the Boltzmann constant. For a set of dipoles with concentration n, the Curie constant would be related with the saturated polarization of the system, P_c, through:

$$C_{c-w} = \frac{4\pi P_c^2}{nk_B} \cdot \qquad (2)$$

Thus, the parameter R defined in (1), can be interpreted as the ratio P_c/P_s between a polarization, P_c, consistent with the observed Curie constant if the system is taken as a set of permanent dipoles and the actual observed saturated polarization, P_s. R can be determined from dielectric data for any ferroelectric material, the only ambiguity

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being the value of n, which depends on the choice of the dipolar unit. Two obvious (in general different) choices are a single molecule or the unit cell. In reference [3] the first choice was made. Here, on the other hand, we will consider the polarization within a unit cell as the basic rigid dipole for equation (2), *i.e.* n is the inverse of the unit cell volume. We consider this second choice more adequate for a comparison with the Φ^4 model which requires a single degree of freedom per unit cell. In the case of several modes (dipoles) per unit cell relevant in the transition, this is equivalent to consider as single mode their linear combination corresponding to the normal mode of lowest energy, this linear combination being directly related to the structural distortion in the transition.

According to its definition, R would be expected to be close to one in order-disorder systems and larger in displacive transitions [1]. This is in accordance with the well-known fact that the Curie constant is typically some orders of magnitude larger in displacive systems. However, although R is proportional to the square root of the Curie constant, a survey of the value of R through well known ferroelectrics indicated a rather small range of values [2]. Indeed, in well known order-disorder systems R is approximately one, but in typical displacive systems only increases up to values of the order of 2 or 3 (see Tab. 1). Tokunaga attributed such small difference to the effect of the long range electrostatic interactions [2]. On the other
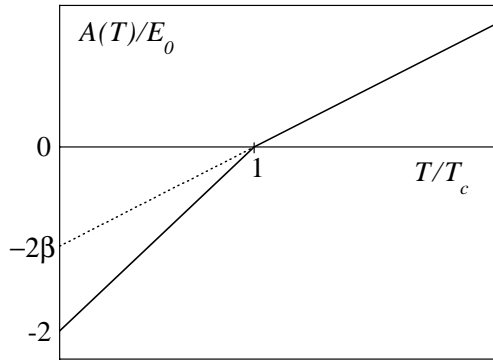
Fig. 1. Idealized scheme of the temperature behaviour of the Landau quadratic coefficient above T_c in the Φ^4 model derived from the results in reference [7] for $C/E_0 = 1$. The dashed line corresponds to the extrapolation to 0 K of the $A(T)$ linear behaviour above T_c.
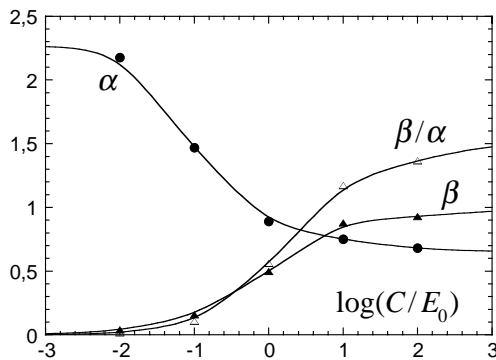

Fig. 2. Behaviour of α, β and α/β as a function of C/E_0 in the Φ^4 model obtained from Monte-Carlo simulations.

hand, some scepticism on the possibilities of the factor R for assessing the order-disorder degree in ferrolectrics has been expressed by Scott [3]. Further discussions can be found in references [4,5].

In the present work Monte-Carlo simulations for the Φ^4 model are used to revise the meaning and relevance of the Rhodes-Wohlfarth factor as a possible empirical parameter measuring the order-disorder degree of ferroelectrics.

The Φ^4 hamiltonian is the simplest model that contains the essential ingredients to describe a rather realistic structural phase transition in the sense that goes beyond the spin (order-disorder) system or the single unstable mode (displacive) picture. The character of the resulting transition can be considered intermediate between the ideal order-disorder and displacive types. It has been widely used for the microscopic description of structural phase transitions, and in particular, ferroelectrics. The Φ^4 hamiltonian can be parameterized so that the ratio between the non-local coupling energy C and the depth of the energy well E_0 is the only free parameter to characterize the system [6,7]. This microscopic parameter governs the order-disorder/displacive degree of the transition, since its two limits (zero and infinity) correspond to the ideal order-disorder and displacive scenarios, respectively,

which in this framework clearly become abstract mathematical limits of the more "realistic" Φ^4 system.

If the empirical parameter R defined by equation (1) would be somehow able to distinguish between order-disorder and displacive systems in the sense that they are closer to one or the other limit, it should be strongly correlated with the mentioned C/E_0 parameter that characterizes the Φ^4 hamiltonian. This correlation is here analysed using the results of Monte-Carlo simulations. Thus, the significance of the Rhodes-Wohlfarth parameter as a signature of the displacive or order-disorder degree of the transition is checked. It will be shown that in general only in rather displacive systems the correlation can be considered significant and can be used to obtain a rough estimation of the energetic parameters of real systems.

2 The Rhodes-Wohlfarth parameter in the 3D Φ^4 model

The Φ^4 model consists of a 3-dimensional lattice of local continuous variables under the influence of local double wells and harmonic couplings with neighbouring sites. The Hamiltonian of the three-dimensional Φ^4 model can be expressed in the form [7]:

$$H = \sum_i E_0 \left(x_i^2 - 1\right)^2 + \frac{1}{2} \sum_i \sum_j^{NN} C \left(x_j - x_i\right)^2. \quad (3)$$

Only nearest-neighbour interactions given by the coupling constant C are considered and E_0 represents the energy barrier between the two local wells for the site variable x. The units of the local variable are normalized to have the minima of the on-site potential at ± 1. Only one parameter in the Hamiltonian (3) is relevant, the other being fixed by the chosen energy units. In fact, the ratio C/E_0 can be taken as a single model parameter and the limits $C/E_0 \to \infty$ and $C/E_0 \to 0$ represent the ideal displacive and order-disorder limits respectively.

The Landau free energy per site for the Φ^4 model can be expressed in the usual form:

$$f = f_0 + AQ^2 + BQ^4 + ... \quad (4)$$

in terms of the normalized order parameter Q given by $Q = (1/N) \sum_i x_i$, which becomes ± 1 in the ground state at $T = 0$ K.

According to recent Monte-Carlo simulations [7] the temperature behaviour of its Landau quadratic coefficient $A(T)$ in equation (4) follows the idealized scheme represented in Figures 1 and 2. In the displacive limit, with C/E_0 much larger than 1, the Landau linear behaviour of the quadratic coefficient is maintained down to the lowest temperatures, so that the extrapolation to 0 K of its linear behaviour above T_c permits a good estimation of the value of $E_0(A(T \to 0) = -2E_0)$, while for smaller values of C/E_0, as the case depicted in Figure 1, the extrapolation of the linear behaviour above T_c underestimates the value of E_0 by the factor β indicated in the figure. This factor β is C/E_0 dependent and follows a smooth
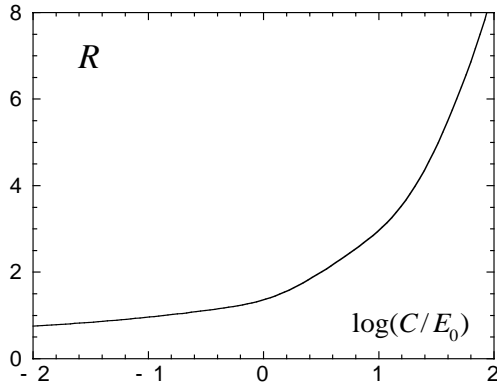
Fig. 3. Rhodes-Wohlfarth factor in the Φ^4 model as a function of the displacive degree C/E_0.

curve (Fig. 2) becoming asymptotically zero and one in the order-disorder and displacive limits, respectively.

Let us now consider the simplest Landau free-energy (per unit volume) for a proper ferroelectric. For a proper comparison with the potential (4) it is necessary to express the usual Landau potential ($f = f_0 + aP^2 + cP^4$) in terms of an analogous normalized order parameter Q defined as P/P_s so that $Q(T = 0) = \pm 1$ irrespective of the displacive or order-disorder character of the transition. Thus,

$$f = f_0 + \frac{1}{2}\frac{4\pi}{C_{c-w}}(T - T_c)P_s^2 Q^2 + \frac{1}{4}bP_s^4 Q^4 \qquad (5)$$

where the expected relationship between the Curie constant and the quadratic coefficient of the potential has been explicitly written. Comparison of the extrapolation for $T = 0$ K of the quadratic coefficients of the two equivalent Landau expansions (4) and (5) for $T > T_c$ gives the relation between the microscopic energetic well (per unit volume) and experimental macroscopic parameters of the ferroelectric:

$$-2E_0\beta(C/E_0) = -\frac{1}{2}\frac{4\pi}{C_{c-w}}T_c P_s^2. \qquad (6)$$

On the other hand, the transition temperature of the Φ^4 model can in general be written as

$$k_B T_c = \alpha(C/E_0)4C \qquad (7)$$

where α is a factor dependent on C/E_0, which varies from 2.275 in the order-disorder limit to 0.65 in the displacive one [6] (see Fig. 2).

From equations (6, 7), taking as unit volume the one associated to the "local mode" or the smallest dipolar unit, the parameter R becomes:

$$R = \sqrt{\frac{C}{E_0}\frac{\alpha}{\beta}}. \qquad (8)$$

Taking the actual behaviour of α and β with C/E_0 from the results in [7] depicted in Figure 2, the variation of the Rhodes-Wohlfarth factor as a function of the displacive degree C/E_0 of the system can be estimated and is shown

in Figure 3. The factor R is slowly varying for small values of C/E_0, since the β approaching zero compensates the decrease of C/E_0. However, in contrast with the arguments in [1,2], the factor can be smaller than one in the order-disorder regime. Close to the displacive limit, for C/E_0 larger than 100, as β approaches 1 asymptotically, the Rhodes-Wohlfarth factor becomes approximately proportional to $\sqrt{C/E_0}$. The factor β is the cause that R maintains a value of the order of one for a large interval of C/E_0 values, while for $C/E_0 \approx 100$, R is still about 5. Hence, one should expect R to be quite insensitive to large differences in C/E_0 when the systems are rather order-disorder as pointed out in reference [4]. Only in the displacive region, when $C/E_0 > 1$, the parameter R may have adequate resolution to assess quantitatively the displacive degree. So in some sense, it would be better to speak of the Rhodes-Wohlfarth factor as a parameter measuring the "displaciveness" of the system. This also explains the limited range of observed values. One should take into account that cases with C/E_0 much larger than 10 are quite improbable: for usual elastic energies, E_0 would be so small that the quantum zero-point energy would be enough to inhibit the phase transition.

3 Discussion

The qualitative features of the results above can be extrapolated to real systems. In the case of interactions between further neighbours and anisotropy of the couplings (J_{ij}) between the local modes at cells i and j, the parameter C can be interpreted as an effective mean coupling given by $C = \frac{1}{3}\sum_j J_{i,j}$ as this is the parameter to be considered in a generalized expression analogous to equation (7) (in the mean field approximation $k_B T_c = 4C$, with C defined in this form [6]). On the other hand, if the Landau hypothesis on the temperature linearity of the quadratic coefficient would be fulfilled for a real system down to 0 K, the same arguments of the previous section would lead to the relation $R = \sqrt{C/E_0}$. Analogously as in the Φ^4 model, this "mean field" relation is to be corrected as in equation (8) by the factors α and β expressing the deviations of T_c and the quadratic Landau coefficient from their mean field/Landau behaviour. Hence, equation (8) can be considered to have a general validity, the parameters α and β taking care of the particularities of each system. In complex systems the variation of α and β with respect to the order-disorder degree of the transition is expected to follow the general trends observed for the Φ^4 model and depicted in Figure 2: the two coefficients α and β should vary smoothly between the two asymptotic values for the order-disorder and the displacive limits (0 and 1 respectively for β). Indeed, some preliminary Monte-Carlo calculations in realistic models with 3-component local order parameters simulating a cubic perovskite confirm this assumption. The resulting Rhodes-Wohlfarth factor R as a function of C/E_0 has the same form as in Figure 3. The actual function for intermediate values may change and depends on the additional parameters of the model, but the asymptotic behaviour at high and low C/E_0 values is maintained.

Table 1. Curie constant, saturated polarization, transition temperature and cell density for representative proper ferroelectrics. Resulting Rhodes-Wohlfarth factor R and estimated values of C/E_0, E_0 and C, derived as explained in the text.

	$C_{c-w}(10^3 \text{ K})$	$P_s(\text{C/m}^2)$	$T_c(\text{K})$	$n(10^{28}\text{m}^{-3})$	R	C/E_0	$C(\text{meV})$	$E_0(\text{meV})$
BiSI	190	0.070	88	0.2700	3.58	16	2.6	0.16
SbSBr	120	0.075	93	0.3127	2.85	9.1	2.6	0.29
$KNbO_3$	242	0.3	435	1.536	2.25	4.4	12	2.7
$BaTiO_3$	173	0.26	393	1.577	2.22	4.2	11	2.6
$Cd_2Nb_2O_7$	100	0.055	185	0.0898	1.91	2.8	4.9	1.8
$LiTaO_3$	1600	0.5	938	0.3173	1.58	1.7	23	14
$PbTiO_3$	410	0.66	763	1.582	1.35	1.0	18	18
SbSI	233	0.25	295	0.2781	1.13	0.33	5.6	17
TGSe	4.05	0.030	295	0.1505	0.91	0.068	4.0	59
TGS	3.20	0.028	321	0.1576	0.89	0.051	4.1	80
$NaH_3(SeO_3)_2$	1.6	0.030	194	0.3441	0.86	0.039	2.4	62
$Pb_5Ge_3O_{11}$	10.4	0.046	450	0.1022	0.78	0.015	4.8	320
TSCC	0.058	0.0027	128	0.06094	0.77	0.012	1.3	110
KNO_3	5.6	0.081	401	0.4194	0.66			
KH_2PO_4	3.1	0.050	123	0.2590	0.63			
TGFB	2.24	0.034	343	0.1573	0.61			
NH_4HSO_4	0.25	0.008	270	0.05662	0.52			
$(NH_4)_2SO_4$	0.029	0.0062	224	0.1768	0.40			

Hence, in general, being aware of the oversimplification and limits of the discussion above, the function in Figure 3 can be used to roughly estimate the C/E_0 value for real materials and using the corresponding functions for α and β (Fig. 2), derive the estimated values of C and E_0. The results for a set of representative proper and pseudo-proper ferroelectrics are shown in Table 1, where the values of Curie constants and saturated polarizations have been taken from reference [3] and most of the compounds listed in this reference have been included. We have, however, excluded clear anomalous cases as Rochelle salt and those ferroelectrics that have an intermediate incommensurate phase. It can be seen that C/E_0 can vary from values as large as 16 in a well known displacive system as BiSI, to values as low as 10^{-4} in typical order-disorder systems as $(NH_4)_2SO_4$, while the parameter R only varies between 0.4 to 3.6. Obviously, as discussed above, these numbers loose ground as one goes into the order-disorder regime, so we have omitted the estimation of E_0 and C for $C/E_0 < 10^{-2}$. Only in the case of rather displacive systems one can expect reasonable results. Indeed, the values of E_0 obtained here for the perovskites can be compared with those predicted by *ab initio* calculations. According to [8], E_0 for $BaTiO_3$, $KNbO_3$ and $PbTiO_3$ would be 15, 11 and 51 meV per unit cell, respectively. The values in Table 1 are systematically smaller but with deviations that do not reach the order of magnitude. For lead titanate, which is the most adequate for the comparison as, in contrast with the other perovskites, it only exhibits a single phase transition with only weak first order character, the estimation of E_0 is closer to the *ab initio* value. The agreement is quite reasonable considering the roughness of the model and the fact that *ab initio* E_0 values are also subject to large uncertainties, as they are quite sensitive to cell parameters which are underestimated by LDA calculations. Changing the cell parameter within its estimated

error can be enough to change the *ab initio* E_0 value by factors as large as 4 or 5 [9].

4 Conclusions

The interpretation of results from Monte-Carlo simulations of the Φ^4 model allows to relate the Rhodes-Wohlfarth parameter (R) and the displacive degree of the transition C/E_0. As the variation of R as a function of C/E_0 is very small for order-disorder systems the parameter R cannot distinguish between quite different order-disorder regimes. On the other hand, in the displacive region, the sensibility of the Rhodes-Wohlfarth parameter to changes of the displacive degree of the transition allows a rough estimation of fundamental microscopic parameters (C, E_0) from experimental macroscopic data.

References

1. M. Tokunaga, J. Phys. Soc. Jap. **56**, 1653 (1987).
2. M. Tokunaga, J. Phys. Soc. Jap. **57**, 4275 (1988).
3. J.F. Scott, J. Phys. Soc. Jap. **58**, 4487 (1989).
4. Y. Onodera, N. Kojyo, J. Phys. Soc. Jap. **58**, 3227 (1989).
5. Y. Onodera, N. Sawashima, J. Phys. Soc. Jap. **60**, 1247 (1991).
6. A.D. Bruce, Adv. Phys. **29**, 111 (1980).
7. S. Radescu, I. Etxebarria, J.M. Perez-Mato, J. Phys.-Cond. Matter **7**, 585 (1995).
8. R.D. King-Smith, D. Vanderbilt, Phys. Rev. B **49**, 5828 (1994).
9. D.J. Singh, L.L. Boyer, Ferroelectr. **136**, 95 (1992).