Study of the phase transitions in lead zirconate by perturbed γ-γ angular correlations*

G. Teisseron and A. Baudry

Departement de Recherche Fondamentale, Centre d'Etudes Nucléaires de Grenoble, B.P. 85, Centre de tri, 38041 Grenoble Cedex, France

(Received 26 August 1974)

The temperature dependence of the electric field gradient on ^{181}Ta substituting Zr atoms in lead zirconate has been studied by time-differential perturbed angular correlations. The existence of an intermediate ferroelectric phase between antiferroelectric and paraelectric phases is confirmed in the (223–233) °C temperature range. Dynamical phenomena near phase transitions, especially in the paraelectric phase, are shown to be present.

INTRODUCTION

It is well established that in ferroelectric or antiferroelectric insulators (like perovskite-type compounds) the electric field gradient (EFG) decreases with increasing temperature and becomes zero when the paraelectric phase is reached. These conclusions follow from local measurements of this EFG by different methods like the Mössbauer effect, time-differential perturbed angular correlation (TDPAC), or nuclear magnetic resonance. More interesting are the dynamical phenomena which appear near phase transitions, typically "soft modes" which may be responsible for the paraelectric-ferroelectric (or antiferroelectric) transitions.[1] These soft modes are usually studied by neutron diffraction, a method restricted to an observable frequency of about 2×10^{12} sec^{-1}. The sensitivity range of TDPAC, for dynamical phenomena, is between 10^6 and 10^{11} sec^{-1}. The aim of this work is to study the possibility of investigating dynamical phenomena near this type of phase transitions by TDPAC.

Lead zirconate presents a structural transition at about 230 °C from the antiferroelectric orthorhombic phase (AF phase) to the paraelectric cubic phase (P phase). X-ray and neutron-diffraction studies at room temperature indicate the existence of two sites for zirconium atoms.[2] Moreover, an intermediate ferroelectric phase (F phase) has been sometimes observed between 200 and 230 °C.[3–6] The temperature range of this F phase depends strongly on sample purity and mechanical treatment.

EXPERIMENTAL METHOD

The lead zirconate used was synthesized from lead oxide (PbO) and radioactive oxychloride ($ZrOCl_2$) containing 1.2-wt% hafnium. PbO and $ZrOCl_2$ analyses data are presented in Table I. Under the same conditions we have produced an inactive synthesis: X-ray measurements have indicated that no excess of ZrO_2 was detectable, within the limit of sensitivity of this method (≈ 5 mole%).

The TDPAC was measured using the 133–482-keV cascade of ^{181}Ta and the time resolution was 2.4 nsec. The heating system had a temperature stability of 0.2 °C at the sample site. The correlation function for ^{181}Ta in a polycrystalline sample is

$$W(\theta, t) = 1 + A_2 G_2(t) P_2(\cos\theta) + A_4 G_4(t) P_4(\cos\theta) . \quad (1)$$

In the particular case of a static electric quadrupole interaction,

$$G_k(t) = s_{k0} + \sum_{l=1}^{3} s_{kl} \cos(\omega_l t) , \quad (2)$$

where the coefficients s_{kl} depend on the asymmetry parameter η defined by $\eta = (V_{xx} - V_{yy})/V_{zz}$, with $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$ (V_{xx}, V_{yy}, V_{zz} are the principal

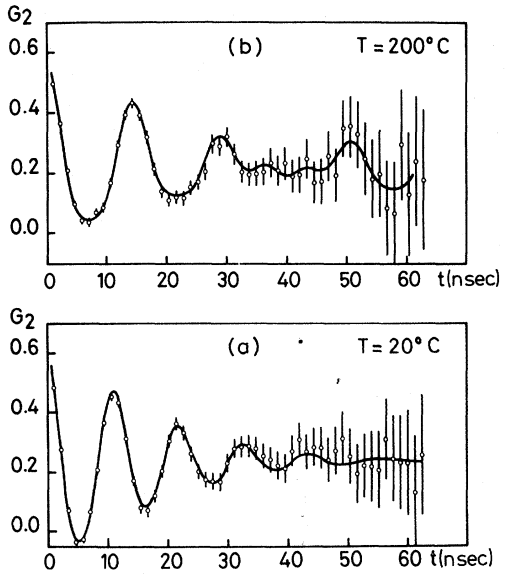

FIG. 1. Perturbed-angular-correlation attenuation of ^{181}Ta in the antiferroelectric phase of $PbZrO_3$ at 20 and 200 °C.

TABLE I. Impurity-analysis data for $ZrOCl_2$ and PbO (weight ppm).

	Na	Mg	Al	Si	K	Ca	Ti	Cr	Fe	Sr	Sn	Ba	Hf
$ZrOCl_2$	<10	<10	80	100	<10	50	<10	<4	100	<10	<10	<10	12 000
PbO	20	40	20	30	20	40	<10	20	<10	<10	<10	<10	<10

EFG components) and the angular frequencies ω_I are functions of η and ω_0, defined by $\omega_0 = 6eQV_{zz}/4I(2I-1)$. Moreover, we have added a Lorentzian frequency distribution (having a width of $\delta = \Delta\omega_0/\omega_0$), which introduces an exponential attenuation $e^{-\delta\omega_I t}$ in each oscillating term in Eq. (2). Corrections for the experimental time resolution were taken into account.

RESULTS

Antiferroelectric phase

Figure 1 shows examples of the time dependence of $G_2(t)$ in the AF phase. Our experimental curves are in good agreement with those published elsewhere.[7,8] In Fig. 2 we have plotted the ω_0 of each EFG as a function of temperature. We observe the usual decrease in ω_0. In fact, to obtain a reasonable χ^2 test $[0.1 \leq P(\chi^2) \leq 0.9]$, we had to introduce two EFG's. Our best fit was obtained with about 50% contribution of the EFG's for each site, in very good agreement with crystallographic results which indicate two nonequivalent zirconium sites.[2] With a single EFG (as used in the previously mentioned articles[7,8]), the fit was too poor to be accepted. A point-charge-model calculation, based on crystallographic data,[6] gives the following values for the EFG parameters of the two sites: $\omega_0 = 550$ and 620 Mrad/sec; $\eta = 0.54$ and 0.52, respectively, at room temperature (with the Sternheimer coefficient $\gamma_\infty = -63$).[9] The temperature dependence of the EFG in the AF phase is fairly well reproduced by this model, indicating that this dependence is mainly caused by the change of lattice parameters and that the covalency bond is nearly constant.

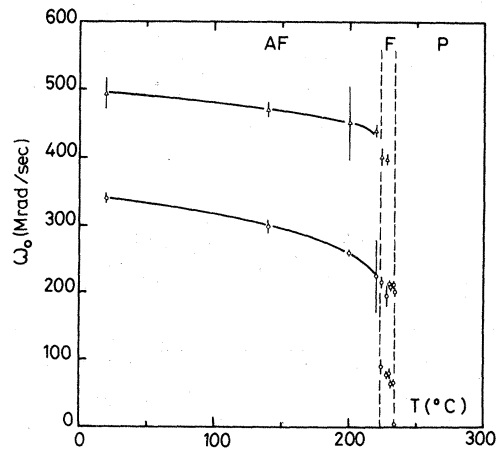

FIG. 2. Temperature dependence of the interaction frequency ω_0 for each EFG in the antiferro- and ferroelectric phases of $PbZrO_3$.

Ferroelectric phase

In Table II are listed the characteristic parameters obtained from best-fit calculations for each EFG. One can observe above 223 °C the apparition of new sites which may indicate a transition into the F phase. A similar behavior of the EFG was recently observed by Einsiedel and Rosenblum.[8] In order to confirm the ferroelectric character of this intermediate phase, we have performed dielectric-constant measurements on our sample. We observe classical thermal hysteresis and slope discontinuity below the transition, due to the presence of an intermediate phase, the ferroelectric character of which was confirmed by the observation of hysteresis loops like the ones detected by Sawaguchi *et al.*[3,10]

Figure 3 shows good correspondence between angular-correlations and dielectric-constant measurements. This F phase is known to be rhombohedral with a unit cell probably a multiple of the

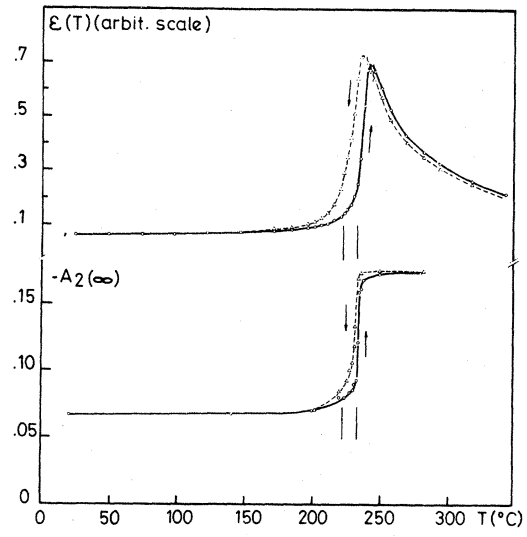

FIG. 3. Comparison of the integral angular-correlation coefficient $A_2(\infty)$ and the dielectric-constant measurement.

TABLE II. Dependence of the EPG parameters on temperature increase in the AF and F phases.

T(°C)	ω_{01} (Mrad/sec)	η_1	δ_1(%)	c_1(%)[a]	ω_{02} (Mrad/sec)	η_2	δ_2(%)	c_2(%)	ω_{03} (Mrad/sec)	η_3	δ_3(%)	c_3(%)
20	490±20[b]	21±0.06	14±4	42±7	340±6	0.89±0.04	6±2	58±7				
140	470±9	0.0±0.1	8±2	43±8	298±9	0.91±0.09	9±2	57±8				
200	490±50	0.0±0.1	120±60	53±4	259±2	0.78±0.10	2±1	47±4				
220	440±8	0.0±0.1	9±2	62±12	220±50	0.91±0.09	30±6	38±12				
224	400±12	0.18±0.1	3±4	18±11	215±8	0.82±0.06	6±4	35±6	90±10	0.0±0.1	8±6	47±11
228	397±7	0.26±0.05	2±2	18±7	195±15	0.98±0.04	6±4	41±7	77±2	0.35±0.06	35±5	40±11
230					212±3	0.75±0.02	4±2	39±6	78±8	0.17±0.30	58±14	61±6
231					209±3	0.74±0.02	5±1	44±3	64±4	0.53±0.18	53±7	56±3
233					211±3	0.73±0.02	5±2	40±5	65±5	0.26±0.23	65±15	60±5

[a] c_i values are the percentages of each EFG. [b] Errors are estimates given by the fit computation.

perovskite subcell, [6] in agreement with our results which seem to suggest the existence of two EFG's.

Paraelectric phase

Zirconium in the P phase, has cubic symmetry and consequently no EFG. In fact, the presence of impurities and lattice defects may introduce symmetry distortions and a low quadrupolar frequency coupling (with a large δ parameter due to local inhomogeneities of defects) can be expected. Actually, the experimental $G_2(t)$ at high temperature (250 °C or higher) is well fitted with $\omega_0 \simeq 13$ Mrad/sec $\eta = 0$, $\delta \simeq 0.4$. Figure 4(a) shows the result of such a fit.

Nearer the F-P transition, $G_2(t)$ has a more abrupt decay which cannot be explained by a low quadrupolar interaction frequency. A good fit can be obtained using the phenomenological formula [Fig. 4(b)] (Table III)

$$G_2(t) = a_0 + a_2 e^{-t/\tau_2}$$

[one can also obtain good fits with this formula for the high-temperature data since with a low frequency and a big δ parameter, $G_2(t)$ is almost equivalent to this last expression]. In Fig. 5 the parameter τ_2 is plotted as a function of decreasing temperature.

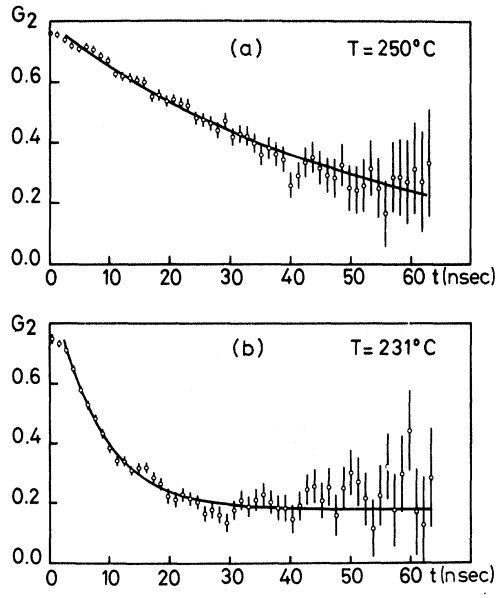

FIG. 4. Perturbed angular correlation attenuation of ^{181}Ta in the paraelectric phase of $PbZrO_3$ at (a) 250 °C: solid line represents the attenuation calculated with a static EFG and $\omega_0 = 13$ Mrad/sec, $\eta = 0$, $\delta = 40\%$. (b) 231 °C: solid line represents the attenuation calculated with $G_2(t) = a_0 + a_2 e^{-t/\tau_2}$.

Dynamical phenomena

In displacive paraferroelectric phase transitions one can expect an optical mode, whose frequency falls to zero when the temperature reaches the critical value T_c. Neutron or x-ray scattering measurements in perovskites are consistent with such a mode. [11] The influence of this mode on the angular-correlation attenuation $G_2(t)$ cannot be described *a priori* by a "spherical-symmetry" theory as in the Abragam and Pound[12] or Andrade[13] models. Consequently, the existence of a hard core in $G_2(t)$ does not exclude the dynamical character of the interaction [for example a strongly anisotropic "fixed-orientation Gaussian-approximation" model[14] gives a hard core for $G_k(t)$].

Furthermore, if we plot $G_2(\infty)$ vs $G_4(\infty)$, the representative points should be in a definite region (hatched area on Fig. 6) if the interaction is a purely static quadrupolar one. Figure 6 shows that in two ranges of temperature the experimental points

TABLE III. Results of the fir of TDPAC attenuation in the P phase by the expression $G_2(t) = a_0 + a_2 e^{-t/\tau_2}$ as a function of decreasing temperature.

T(°C)	a_0	a_2	τ_2 (nsec)
250	0.07±0.10[a]	0.74±0.10	45.5±10
236	0.13±0.09	0.67±0.09	40.0±9.5
234.5	0.19±0.05	0.63±0.05	27.8±4.5
233	0.22±0.01	0.60±0.01	11.4±6.5

[a] See footnote b of Table II.

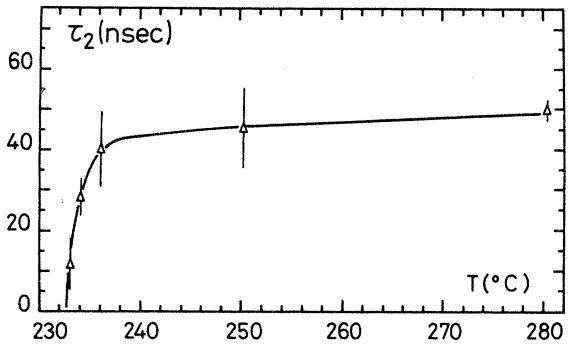

FIG. 5. Mean time τ_2 of the exponential attenuation of $G_2(t)$ in the paraelectric phase as a function of decreasing temperature.

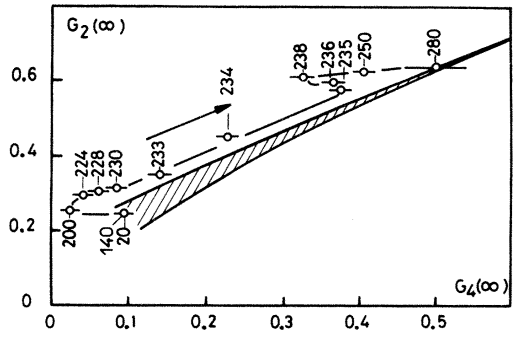

FIG. 6. Plot of the integral coefficient $G_2(\infty)$ vs $G_4(\infty)$. Hatched area is the region allowed by a purely static quadrupolar interaction. Errors on $G_2(\infty)$ are smaller than the points in the figure.

fall significantly off the static area. In the range (200–223) °C, this corresponds to too big δ values of the $G_2(t)$ fits and in the 235 °C region to the abrupt variation of the τ_2 parameter.

CONCLUSION

The perturbed-angular-correlation method seems to be suitable for studies of EFG variations in the different phases of perovskite-type crystals. Furthermore, this method is sensitive to dynamical phenomena near the phase transitions in $PbZrO_3$ [and probably in $PbHfO_3$ in which Forker had observed a strong damping of $G_2(t)$ near the transition[15]].

It should be possible to obtain information about the temperature dependence of optical modes in these compounds by TDPAC performed on single crystals and using a longer-lived intermediate-state nucleus as a probe. Such measurements are in preparation.

ACKNOWLEDGMENTS

We are indebted to Professor J. Lajzerowicz for helpful discussions and to Dr. J. C. Peuzin for encouraging our dielectric-constant measurements. We wish to thank Professor J. I. Vargas who suggested the subject of this work.

*Work is part of a thesis in Solid State Physics presented by one of us (G.T.) at the Université Scientifique et Médicale de Grenoble, June 1973.

[1]W. Cochran, Adv. Phys. 9, 387 (1960).

[2]F. Jona, G. Shirane, F. Mazzi, and R. Pepinsky, Phys. Rev. 105, 849 (1957).

[3]E. Sawaguchi, G. Shirane, and Y. Tagaki, J. Phys. Soc. Jpn. 6, 333 (1951).

[4]G. Shirane, E. Sawaguchi, and Y. Tagaki, Phys. Rev. 84, 476 (1951).

[5]V. J. Tennery, J. Electrochem. Soc. 112, 1117 (1965).

[6]V. J. Tennery, J. Am. Ceram. Soc. 49, 483 (1966).

[7]M. Forker and A. Hammesfahr, Z. Phys. 255, 196 (1972).

[8]H. V. Einseidel and S. S. Rosenblum, Proceedings of the International Conference on Hyperfine Interactions Studied in Nuclear Reactions and Decay, Uppsala, June, 1974 (unpublished).

[9]F. D. Feiock and W. R. Johnson, Phys. Rev. 187, 39 (1969).

[10]E. Sawaguchi, J. Phys. Soc. Jpn. 8, 615 (1953).

[11]R. Comes, F. Denoyer, and M. Lambert, J. Phys. (Paris) 32, 195 (1971).

[12]A. Abragam and R. V. Pound, Phys. Rev. 92, 943 (1953).

[13]P. da R. Andrade, J. D. Rogers, and A. Vasques, Phys. Rev. 188, 571 (1969).

[14]F. Bosch and H. Spehl, Z. Phys. 253, 257 (1972).

[15]M. Forker, A. Hammesfahr, A. Lopez-Garcia, and B. Wolbeck, Phys. Rev. B 7, 1039 (1973).