

ELECTRIC QUADRUPOLE INTERACTIONS IN THE CdTiO₃ PEROVSKITE†

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Abstract—The TDPAC technique has been used to measure the EFG at the Cd site in the perovskite CdTiO₃. The experimental results obtained at 293 K are compared with ionic lattice sum calculations of the EFG. In addition measurements at 16 and 77 K show that no considerable modification of the EFG is observed at the Cd site at temperatures below and above the previously described phase transition at 50 K.

1. INTRODUCTION

The number of simple ferroelectrics and antiferroelectrics of the oxygen-octahedral type is small. Consequently the synthesis of CdTiO₃ and the observation of its properties is of considerable interest. A comparison between the properties of cadmium and the best-studied lead perovskites is also of interest.

The ferroelectric perovskite-type compound CdTiO₃ has been investigated by various techniques such as X-ray diffraction[1, 2], temperature and pressure dependence of the dielectric constant[3] and infrared spectroscopy[4]. A considerable amount of information has been obtained from these measurements concerning the crystal structure, phase transitions and dielectric properties.

Another quantity of great interest is the internal electric field gradient (EFG). Since the EFG reflects the microscopic charge distribution, its determination, and especially the investigation of its temperature dependence, should give valuable information about the crystal. In fact, measurements of the EFG have proved to be a very useful tool for the understanding of the microstructure of the antiferroelectric lead perovskites PbHfO₃[5] and PbZrO₃[6].

In order to extend this kind of investigation to the cadmium perovskites we have performed a series of precise measurements of the EFG acting on ¹¹¹Cd nuclei in CdTiO₃ using the time-differential perturbed angular correlation (TDPAC) method.

2. ANGULAR CORRELATION MEASUREMENTS

The TDPAC of two successive γ -rays in a nuclear sequence measures directly the interactions between the nuclear moments of the intermediate state and the hyperfine field acting at the nucleus. Assuming only static quadrupole interaction oriented randomly in space and a nuclear level with spin $I = (5/2)$ the angular cor-

relation can be expressed by:

$$W(\theta, t) = A_0 + A_{22}G_{22}(t)P_2(\cos \theta) + A_{44}G_{44}(t)P_4(\cos \theta)$$

where the perturbation factor $G_{kk}(t)$ is given by:

$$G_{kk}(t) = \sigma_{k0} + \sum_{n=1}^k \sigma_{kn} \cos(\omega_n t) \exp\left(-\frac{\delta}{2} \omega_n t\right).$$

The amplitudes σ_{kn} and the frequencies ω_n depend on the nuclear quadrupole frequency

$$\omega_Q = \frac{e^2 Q V_{zz}}{4I(2I-1)}$$

and on the asymmetry parameter of the EFG tensor

$$\eta = \frac{|V_{yy} - V_{xx}|}{|V_{zz}|}$$

The term $[-(\delta/2)\omega_n t]$ gives the Lorentzian distribution of frequencies having a half width at half maximum of $\delta\omega_n$. This means that the measurement of the $G_{22}(t)$ perturbation factor contains information on the magnitude of the maximal component of the EFG V_{zz} acting at the nucleus, its asymmetry η (essentially a geometry dependent parameter) and the degree of spreading δ of the EFG. The PAC formalism for static interactions is described in Ref. [7].

The polycrystalline CdTiO₃ perovskite was prepared by the following procedure. CdO and TiO₂ were mixed in the stoichiometric ratio, pressed into a pellet and sintered at 1000°C for 12 hr in a CdO atmosphere in order to prevent the sublimation of cadmium oxide. The sample was subjected to X-ray diffraction analysis to confirm the structure.

The radioactive probe nuclei were obtained by proton irradiating the CdTiO₃ sample, thus forming ¹¹¹In through the ¹¹¹Cd(p, n) ¹¹¹In reaction. The ¹¹¹In activity with half life $T_{1/2} = 2.8$ d decays by electron capture

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populating nuclear levels in ^{111}Cd . We have measured the $A_{22}G_{22}(t)$ coefficients for the 247 keV level (spin $I = (5/2)$ and $T_{1/2} = 84$ nsec) in ^{111}Cd via the 173–274 keV cascade. The experimental results for temperatures of 293, 77 and 16°K are shown in Fig. 1, and the parameters extracted by computer fits are displayed in Table 1.

In order to check the lattice position of the probe nuclei produced by the (p, n) reaction in CdTiO_3 , the sample was annealed for 48 hr at 1000°C to eliminate possible radiation damage and the $A_{22}G_{22}(t)$ coefficient was measured again, giving the same result as before annealing. This means that the ^{111}In ions are not displaced from the lattice positions and that at the time when the γ -rays are emitted, the ^{111}Cd ions stay at regular lattice sites. As an additional proof of this point we have performed a second experiment which consisted of neutron irradiating the CdTiO_3 , and producing by the reaction $^{110}\text{Cd}(n, \gamma)^{111m}\text{Cd}$ the isomeric state at 397 keV in ^{111}Cd with $T_{1/2} = 49$ m. This state decays through the cascade 150–247 keV via the same 247 keV level. The $A_{22}G_{22}(t)$ coefficient measured for this cascade is shown in Fig. 2, where the fitting was performed using the same ω and η obtained from the proton irradiated sample at

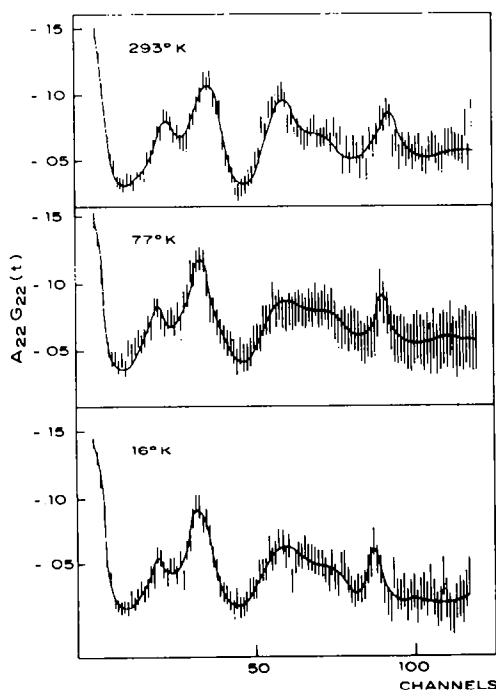


Fig. 1. $A_{22}G_{22}(t)$ coefficients at the ^{111}Cd site in CdTiO_3 for the proton irradiated sample. Calibration: 2.3 nsec/channel.

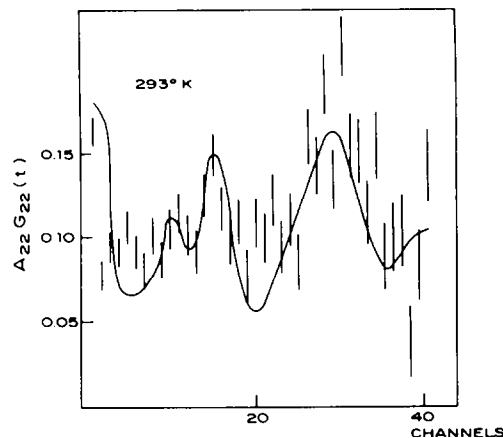


Fig. 2. $A_{22}G_{22}(t)$ coefficient at the ^{111}Cd site in CdTiO_3 for the neutron activated sample. Calibration: 5 nsec/channel.

293°K (see Table 1). A larger $\delta = 0.08\%$ was used in this fitting. Due to the short half life of the isomeric state, it is difficult to perform a precise experiment, with good statistics, but within the errors the results are the same as for the proton-produced sample.

Using for the nuclear quadrupole moment of the 247 keV state the value of $Q = 0.77(12)b$ [8] we obtain the experimental values of the maximal component of the EFG V_{zz} for the three measured temperatures. The results are in Table 1.

3. DISCUSSION

From X-ray diffraction studies [2] the following facts have been established:

(a) CdTiO_3 has orthorhombic symmetry with four molecules in the unit cell and lattice parameters $a = 5.348 \text{ \AA}$, $b = 7.615 \text{ \AA}$ and $c = 5.417 \text{ \AA}$ (see Fig. 1 in Ref. [2]).

(b) Three space groups were considered for the crystal, namely $Pcmm(1)$, $Pcmm(2)$ or $Pc2_1n$.

(c) The space group $Pcmm(1)$ was readily eliminated by consideration of the $(0kl)$: k odd, l even, class of reflections.

(d) It is not possible to eliminate easily either of the two other space groups. Even so, the maximum possibilities of the technique were explored in order to establish the ion displacements in the orthorhombic structures and to find the real space group. The result was to propose the $Pc2_1n$ space group for CdTiO_3 and to establish the position of each ion in the unit cell (see Table 4 and Fig. 2(a) in Ref. [2]).

Table 1. Experimental parameters extracted from the fitting of the $A_{22}G_{22}(t)$ curves at the Cd site, and calculated V_{zz} and η for two different structures of CdTiO_3 (see text)

T (°K)	ω_1 (MHz)	Experimental		V_{zz} (10^{17} V/cm^2)	Space group	Calculated	
		η	δ			V_{zz} (10^{17} V/cm^2)	η
293	16.04 ± 0.08	0.407 ± 0.008	0.057 ± 0.005	5.41 ± 0.80	$Pc2_1n$	8.16	0.83
77	16.98 ± 0.17	0.428 ± 0.013	0.051 ± 0.009	5.71 ± 0.83	$Pcmm(2)$	9.05	0.39
16	17.20 ± 0.07	0.437 ± 0.006	0.053 ± 0.005	5.80 ± 0.81			

As a first step in the analysis of our results we performed a calculation of the ionic EFG acting at Cd nuclei in CdTiO₃ by the lattice sum method[9]. In this calculation we included the monopole and dipole contribution to the EFG using the ion positions of the space group $Pc2_1n$ proposed by Kay and Miles[2], the nominal charges, the electric dipole moment of each ion in the unit cell as given in Ref. [10] and the Sternheimer antishielding factor $1 - \gamma_\infty = 30$ [11]. The dipole contribution is small compared to the monopole contribution in the case of CdTiO₃. The result of this calculation is

$$V_{zz}^{\text{calc}} = 8.16 \times 10^{17} \frac{V}{\text{cm}^2}, \eta^{\text{calc}} = 0.83.$$

These values are to be compared with the experimental results at room temperature (see Table 1).

The discrepancy between the calculated and the experimental values of the EFG can be, in principle, attributed to the departure of the real structure from the structure used in the calculation and to the covalency contribution to the EFG. As demonstrated before[12–14], X-ray techniques alone do not necessarily yield the structure of these distorted perovskites. Some studies have been successful only when X-ray information was supplemented by neutron scattering data. Moreover, in the case of EFG measurements at the Hf sites in PbHfO₃ and PbZrO₃, whose structures are very well known from combined X-ray and neutron diffraction experiments, Forker *et al.*[5,6] have obtained very good agreement between the experimental values of η and the values obtained with point charge lattice sum calculations in spite of the disagreement between the experimental and calculated V_{zz} values. This indicates that a covalency contribution to the EFG is present in these compounds and that it is isotropic.

In a second calculation we have taken the $Pc2_1n$ space group. This space group was eliminated by Kay and Miles[2] on the basis of X-ray diffraction measurements but, as we mentioned before, the elimination of this space group using only X-ray techniques is not conclusive. The ionic shifts permitted by the $Pc2_1n$ and $Pc2_1n$ space groups are very similar except that $Pc2_1n$ imposes certain restrictions on the displacements. We have imposed these restrictions and conserved the ionic displacements determined by Kay and Miles which are common to the two space groups. For the y displacements of the O₂ and O₃ ions we have taken, arbitrarily, values of -0.03 and $+0.03$ respectively. The positions of the various ions are shown in Table 2. With this structure we have obtained:

$$V_{zz}^{\text{calc}} = 9.05 \times 10^{17} \frac{V}{\text{cm}^2}, \eta = 0.39.$$

We note from this result the very good agreement between the experimental and calculated values of η and, again, the existence of an essential covalency contribution to V_{zz} . Unfortunately the sign of V_{zz} was not measured. Assuming a positive sign for V_{zz} , the covalency contribution must be of the order of 40% of

the ionic contribution with opposite sign. As V_{zz}^{calc} is larger in modulus than the experimental value, it means that in CdTiO₃, the covalent contribution to V_{zz} has an opposite sign to that of the ionic contribution, independently of the sign of V_{zz} .

So, assuming that the covalent contribution to the EFG at the Cd site in CdTiO₃ is also isotropic, this analysis indicates that the space group $Pc2_1n$ is able to account for the experimental results and has to be taken into account in the description of the structure of CdTiO₃.

It is very interesting to point out that this configuration for the structure of CdTiO₃ was suggested by Megaw[1], who claimed that because the Cd ion is held by weaker electrostatic bond strength in the structure (2/12 for the Cd–O bond as compared with 4/6 for Ti–O), it seems likely that the cadmium ions are displaced and the Ti ions are undisplaced or have very small displacements. This tendency, reinforced by oxygen displacements, brings the Cd ion closer to six of its neighbouring oxygens and further away from the other six, resulting in a 6-coordination for the Cd ion which is more appropriate to its radius. Using the data of Table 2, it is easy to verify that the Cd ions have six nearest neighbour oxygens in this structure.

Finally, we consider the phase transition at 50 K[3]. It was suggested by Smolenskii[15] that this is a transition from the ferroelectric to the paraelectric state.

Table 2. Ionic positions in CdTiO₃ used in the lattice sum calculation of the EFG with the space group $Pc2_1n$

	$x: 0 + 0.006$	$0 - 0.006$	$\frac{1}{2} + 0.006$	$\frac{1}{2} - 0.006$
Cd	$y: \frac{3}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$
	$z: 0 + 0.016$	$0 - 0.016$	$\frac{1}{2} - 0.016$	$\frac{1}{2} + 0.016$
	$x: \frac{1}{2}$	$\frac{1}{2}$	0	0
Ti	$y: 0$	$\frac{1}{2}$	$\frac{1}{2}$	0
	$z: 0$	0	$\frac{1}{2}$	$\frac{1}{2}$
	$x: 0 - 0.03$	$0 + 0.03$	$\frac{1}{2} + 0.03$	$\frac{1}{2} - 0.03$
O ₁	$y: \frac{3}{4}$	$\frac{1}{4}$	$\frac{3}{4}$	$\frac{1}{4}$
	$z: \frac{1}{2} + 0.05$	$\frac{1}{2} - 0.05$	$0 + 0.05$	$0 - 0.05$
	$x: \frac{1}{4} + 0.05$	$\frac{1}{4} - 0.05$	$\frac{3}{4} - 0.05$	$\frac{3}{4} + 0.05$
O ₂	$y: 0 - 0.03$	$0 - 0.03$	$\frac{1}{2} - 0.03$	$\frac{1}{2} - 0.03$
	$z: \frac{1}{4} + 0.06$	$\frac{3}{4} + 0.06$	$\frac{3}{4} - 0.06$	$\frac{1}{4} - 0.06$
	$x: \frac{1}{4} + 0.05$	$\frac{1}{4} - 0.05$	$\frac{3}{4} - 0.05$	$\frac{3}{4} + 0.05$
O ₃	$y: \frac{1}{2} + 0.03$	$\frac{1}{2} + 0.03$	$0 + 0.03$	$0 + 0.03$
	$z: \frac{1}{4} + 0.06$	$\frac{3}{4} + 0.06$	$\frac{3}{4} - 0.06$	$\frac{1}{4} - 0.06$

The experimental $A_{22}G_{22}(t)$ coefficients obtained at 16 and 77 K have similar values and there is no large variation of V_{zz} and η observed at the Cd sites (see Table 1). The small decrease of V_{zz} and η from 16 to 77 K is due to lattice expansion and/or vibration.

We would like to comment on this result, noting initially that CdTiO₃ is a displacive ferroelectric, and that a transition from the ferroelectric to the paraelectric state in this class of ferroelectrics is, in general, accompanied by a change in the symmetry of the crystal. This is the case of BaTiO₃, PbHfO₃ and PbZrO₃. On the other hand, earlier measurements of TDPAC [5, 6, 16] in these compounds showed that a symmetry change of the crystal causes a drastic variation of V_{zz} and η . Although all these measurements were made with the probe nucleus (¹⁸¹Ta) at the position of the B ions (Ti, Zr, Hf) in these ABO₃ perovskites, we would also expect that a symmetry change in CdTiO₃ would cause a drastic variation of the EFG at the ¹¹¹Cd probe nucleus which occupies the site of an A ion. If this is really the case, then the experimental results indicate that there is no symmetry modification around 50 K, and the phase transition is probably a transition from one ferroelectric state to another analogous to the antiferro-antiferroelectric phase transitions in PbHfO₃ at 163°C [17] and CdHfO₃ at 605°C [18, 19]. This is not a conclusive argument, not only because there could be a symmetry change which does not cause a drastic variation of the EFG at the Cd site, but also because even if the symmetry change occurs at 50°K it still can be a transition from one ferroelectric state to another.

The nature of the phase transition at 50 K in CdTiO₃ has been discussed by Lyubimov *et al.* [10], who claimed that this may be a transition from one ferroelectric state to another.

4. SUMMARY

In this paper we report precise TDPAC measurements at the Cd site in the ferroelectric perovskite-type compound CdTiO₃.

The experimental values at room temperature of V_{zz} , the maximal component of the EFG, and η , the asymmetry parameter, are compared with ionic lattice sum calculations. The comparison between the experimental and calculated values indicates the existence of an essential covalency contribution to the EFG. Assuming that this contribution is isotropic, good agreement with the experimental result is obtained if we describe the

structure of CdTiO₃ by the space group *Pcmn*(2) and if we admit a covalency contribution to V_{zz} which is of the order of 40% of the lattice sum contribution and has opposite sign. A weak point of this conclusion is that we do not measure the sign of V_{zz} , which was assumed positive. However, independently of the sign of V_{zz}^{exp} , the covalency contribution to V_{zz} has an opposite sign to the lattice sum contribution.

We have also measured the TDPAC at 77 and 16 K. Only a small change in V_{zz} and η at the Cd sites was observed between these temperatures. This result is discussed in terms of previous measurements of TDPAC in perovskite-type compounds and a reported ferroelectric phase transition in CdTiO₃ at 50 K.

Measurements of TDPAC at the Ti site in CdTiO₃ and calculations of the covalency contribution to the EFG are in progress.

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