Hyperfine Interactions 4 (1978) 615-621
North-Holland Publishing Company

TEMPERATURE DEPENDENCE OF ELECTRIC FIELD GRADIENTS AT Cd AND Hf SITES IN CADMIUM PEROVSKITES

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1. INTRODUCTION

The time-differential perturbed angular correlation (TDPAC) technique was used to measure the electric field gradient (EFG) and its temperature dependence in ferroelectric perovskite-type compounds of cadmium. The number of simple ferro and antiferroelectrics of the oxygen-octahedral type is small, consequently the synthesis of the compounds $CdXO_3$ (X = Ti, Zr, Hf, Sn) and the observation of its properties is of large interest. A comparison between the properties of the cadmium and the best studied lead perovskites is also of considerable interest.

Since the EFG reflects the microscopic charge distribution, its determination and specially the investigation of its temperature dependence should give valuable information about the properties of these compounds. The experimental results are analyzed in terms of the structural and electric properties of cadmium perovskites which are members of the displacive class of ferroelectrics.

We measured the angular correlation attenuation coefficients $A_{22}(t) = A_{22}(0)G_{22}(t)$ where

$$G_{kk}(t) = \sum_n \sigma_{kn} \cos(\omega_n t) \exp(-\frac{\delta\omega_n t}{2}) .$$

The amplitudes σ_{kn} and the frequencies ω_n are related to the quadrupole interaction frequency ω_Q and to the asymmetry parameter η 1). From the quadrupole interaction frequency, using the known values of the electric quadrupole moments of the nuclear states, we extracted the maximal component V_{zz} of the EFG.

2. TDPAC OF ^{111}Cd IN $CdTiO_3$

The ferroelectric perovskite-type compound of $CdTiO_3$ has been investigated by various techniques such as X-rays diffraction 2,3), temperature and pressure dependence of the dielectric constant 4) and infrared spectroscopy 5). Considerable amount of information has been obtained but some important properties of the crystal concerned to its structure, extent of the covalent bonding and the nature of a phase transition at 50K are not well established.

With the intention of clarifying the above points we performed a series of precise measurements of the EFG acting on ^{111}Cd nuclei in $CdTiO_3$ using the TDPAC technique. The radioactive probe is ^{111}In obtained by irradiating the sample with protons to produce the reaction ^{111}Cd (p,n)^{111}In. ^{111}In decays by electron capture to ^{111}Cd and the measurements were done using the intermediate state at 247 keV ($I = 5/2$, $T_{1/2} = 84$ ns) in ^{111}Cd. The quadrupole moment of this state is $Q = 0.77(12)b^{6)}$. The $CdTiO_3$ sample was prepared following the method described in ref. 7.

The experimental $A_{22}(t)$ curves for temperatures of 293, 77 and 16 K are shown in fig. 1. The parameters extracted by computer fits of the experimental data are displayed in table 1.

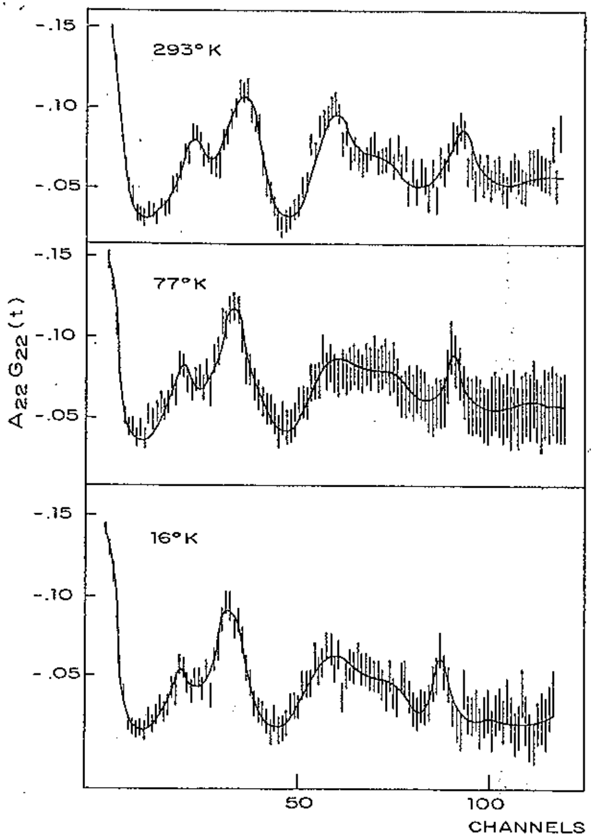

Fig. 1 - $A_{22}G_{22}(t)$ coefficients at the Cd site in $CdTiO_3$. Calibration: 2.3 ns/channel.

We have performed an ionic lattice sum calculation of the EFG using two possible structures for $CdTiO_3$, namely the $Pc2_1n$ and Pcmn(2) space groups. In this calculation we included the monopole and dipole contributions, using the induced electric dipole moment of each ion given in ref. 8. The ion positions in the unit cell for the $Pc2_1n$ space group are given in ref. 2, and since the ion shifts permitted by the two space groups are very similar except that Pcmn(2) imposes certain restrictions, the ion positions in this space group are readily established. The calculation showed that the dipole contribution to the EFG in $CdTiO_3$ is small compared with the ion contribution.

Table 1 - Experimental and calculated values for V_{zz} and η at Cd site in $CdTiO_3$

Experimental					Calculated		
T (^{o}K)	ω_1 (MHz)	η	δ	V_{zz} (10^{17}V/cm^2)	Space group	V_{zz} (10^{17}V/cm^2)	η
293	16.04(8)	0.407(8)	0.057(5)	5.41(6)	$Pc2_1n$	8.16	0.83
77	16.98(9)	0.428(9)	0.051(9)	5.71(8)	Pcmn(2)	9.05	0.39
16	17.20(7)	0.437(6)	0.053(5)	5.80(6)			

We note that V_{zz}^{calc} for both possible structures of $CdTiO_3$ is larger than V_{zz}^{exp}; this is mainly due to the fact that the covalent bonding has not been taken into account in the calculation. On the other hand η^{calc} for the Pcmn(2) space group reproduces very well the experimental result whereas for the $Pc2_1n$ space group it is a factor of 2 larger than the experimental value. Since η depends mainly on the symmetry of the lattice, this result indicates that the Pcmn(2) space group is the best assignment for the structure of $CdTiO_3$ and so the ferroelectricity of this perovskite is due to the distortion described by this space group.

Unfortunately the sign of V_{zz}^{exp} was not measured. Assuming a positive sign for V_{zz}^{exp} the agreement between the experimental and the calculated values is obtained if we admit that the covalent contribution to V_{zz} is of the order of 40% of V_{zz}^{calc} and of opposite sign. This is consistent with the results obtained in many other perovskites like $PbHfO_3$ 9), $PbZrO_3$ 10), $PbTiO_3$ and $BaTiO_3$ 11).

The small decrease of V_{zz}^{exp} and η^{exp} from 16 to 77^{o}K is due to lattice expansion and/or vibration. Usually a change in the structure of the crystal gives a drastic variation of V_{zz} and η 9,10,11). So, this result indicates that the phase transition at 50^{o}K 4) is not accompanied by a structural change and since $CdTiO_3$ is a displacive ferroelectric it is very probably a transition from one ferroelectric state to another as suggested by Lyubimov et al. 8).

As an extension of the results presented above we also report measurements of the EFG at the Cd site in $CdXO_3$ (X = Ti, Zr, Hf and Sn) perovskite-type compounds. Here the TDPAC measurements were made by irradiating the samples with neutrons to produce the reaction $^{110}Cd(n,\gamma)^{111m}Cd$ and so populate the isomeric state at 397 keV in ^{111}Cd with $T_{1/2}$ = 49 min. This state decays through the cascade 150-247 keV via the same 247 keV level used in the measurements reported above. Due to the short half-life of the isomeric state the statistics is poor and only room temperature measurements could be done. The $A_{22}(t)$ coefficients are shown in fig. 2.

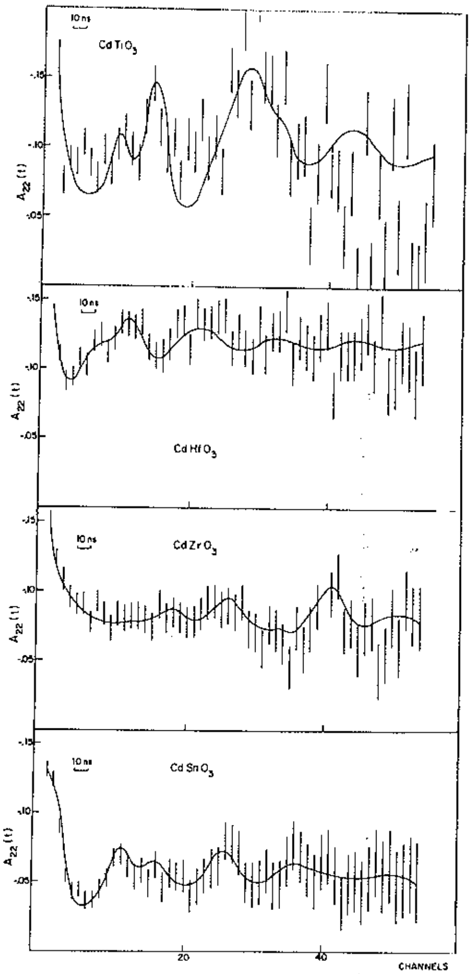

Fig. 2 - $A_{22}G_{22}(t)$ coefficients at the ^{111}Cd site in $CdXO_3$ perovskites. Neutron activated samples. Calibration: 5ns/channel.

In table 2 are displayed the parameters extracted from the fittings, the values of V_{zz}^{exp} for each compound and the V_{zz}^{calc} and η^{calc} values obtained using the lattice parameters of each compound. We note that:

a) the data for $CdTiO_3$ confirm the measurement done with the proton irradiated sample;

b) the calculation for V_{zz} and η at Cd site in $CdHfO_3$ made with the ion positions given by the Pcmn(2) space group fits reasonably well the experimental results, indicating that the structure of this perovskite is similar to the structure of $CdTiO_3$;

c) for $CdZrO_3$ and $CdSnO_3$ the values of V_{zz}^{calc} and η^{calc} with the two space groups $Pc2_1n$ and Pcmn(2) do not agree with the experimental values. This results indicate a large departure of the structure of these perovskites from the two space groups proposed by Kay and Miles for the structure of $CdTiO_3$.

Table 2 - Experimental and calculated values of V_{zz} and η at Cd site in cadmium perovskites (neutron irradiated samples)

	Experimental			Calculated			
				$Pc2_1n$		Pcmn(2)	
Perovskite	ω_1 (MHz)	V_{zz} $(10^{17}\frac{V}{cm^2})$	η	V_{zz} $(10^{17}\frac{V}{cm^2})$	η	V_{zz} $(10^{17}\frac{V}{cm^2})$	η
$CdHfO_3$	17.3(7)	6.1(2)	0.35(5)	7.6	0.78	8.0	0.32
$CdZrO_3$	10.0(8)	3.3(4)	0.46(12)	4.0	0.56	7.5	0.35
$CdSnO_3$	17.9(4)	6.3(3)	0.57(5)	7.4	0.72	8.15	0.32

3. TDPAC OF ^{181}Ta IN $CdHfO_3$

The EFG acting at the Hf(Ta) site in $CdHfO_3$ was measured as a function of temperature to investigate the phase transitions in this compound. The preparation of the sample was made following the method described in ref. 7.

Previous results obtained studying dielectric and optical properties indicate that $CdHfO_3$ exhibits antiferroelectric properties$^{12)}$. Two phase transitions were detected at 878 and 993°K. Another phase transition was reported by Aver'yanova et al.$^{7)}$ at 288 K.

The TDPAC measurements were done using as radioactive probe the nucleus of ^{181}Hf which decays to ^{181}Ta populating the well known 133-482 keV γ-γ cascade. The experimental $A_{22}(t)$ coefficients for four typical temperatures are shown in fig. 3. The solid lines represent best fits with theoretical expressions.

In figs. 4-a and 4-b we show the complete set of V_{zz}^{exp} and η^{exp} as a function of temperature ($Q = 2.53\pm0.10b^{13)}$ was used for the 482 keV state of ^{181}Ta).

We note that V_{zz}^{exp} has a smooth variation around 878°K and the asymmetry parameter has a very well defined increase at this point. At 993°K V_{zz}^{exp} and η^{exp} have a sharp variation, both decreasing by a factor of 4. Many factors influence the V_{zz} and η dependence with temperature. We mention here the temperature dependence of the lattice parameters, the variation it causes in the volume of the perovskite cell and the dipole rearrangement close to the critical temperatures.

Figure 3

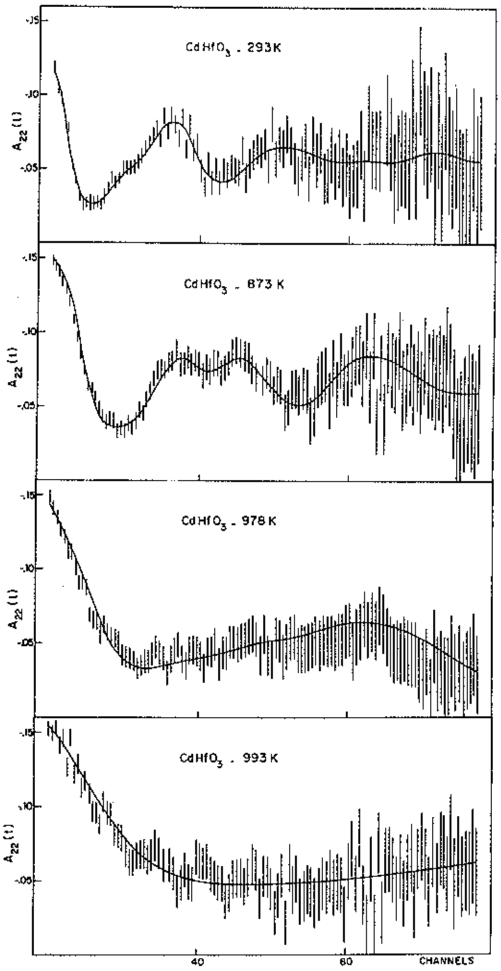

Figure 4

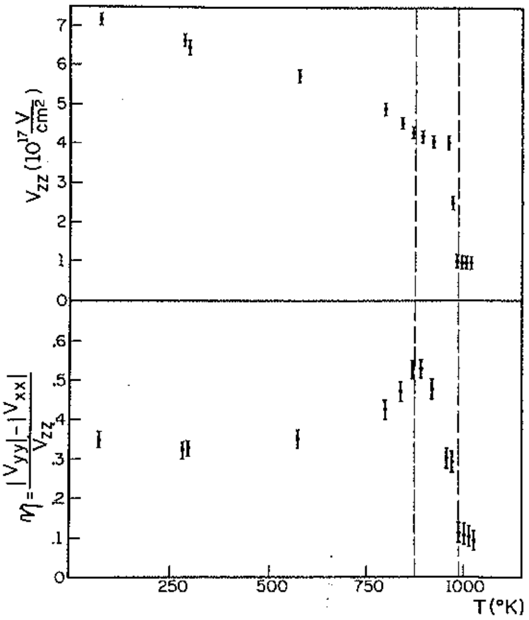

Fig. 3 - $A_{22}G_{22}(t)$ coefficients at the ^{181}Ta site in CdHfO$_3$. Calibration: 0.48 ns/channel.

Fig. 4 - V_{zz} and η as a function of temperature in CdHfO$_3$.

The temperature dependence of the lattice parameters of CdHfO$_3$ was studied by Spinko et al.[12]. This work establishes definitively the existence of two high-temperature phase transformations at 878±15°K and 993±5°K. The first transformation from the orthorombic phase I into the orthorombic phase II is characterized by an increase in the volume of the reduced perovskite cell. The second phase transformation is accompanied by a sharp change in the volume of the perovskite cell and a change in its symmetry from orthorombic II to the rhombohedral phase. There is no structure change at 288°K.

We have performed a point charge lattice sum calcularion using CdHfO$_3$ lattice parameters and assuming that the structure of CdHfO$_3$ is similar to that of CdTiO$_3$ discussed in the previous section. At room temperature we obtain $V_{zz}^{calc} = 27\times10^{17} V/cm^2$ and $\eta^{calc} = 0.33$. The variation of V_{zz}^{calc} with temperature estimated using the data of reference 12 is much smaller than the experimental one. The variation of η^{calc} with temperature, on the other hand, agrees reasonably with the experimental results.

The discrepancy between V_{zz}^{exp} and V_{zz}^{calc} is certainly due to the dipolar and covalent contributions to V_{zz} (a detailed study of this problem is under progress).

We did not observe any change in V_{zz}^{exp} and η^{exp} around 288°K, in agreement with the X-ray data of Spinko et al.12).

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