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Ferroelectric properties of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ solid solutions

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Measurements of the spontaneous polarization P , x-ray diffraction, birefringence, dielectric constant at different frequencies, and specific heat C_p of the $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}$ alloy are presented. The results demonstrate that this system exhibits a diffuse, second-order ferroelectric transition. The transition is of order-disorder type as deduced from the dielectric measurements. It is found that: (a) The birefringence is proportional to P , as expected from a system with a piezoelectric paraelectric phase; (b) the heat capacity is given by $C_p = (T_c/C) |(PdP/dT)|$, where C is the Curie constant. One of the main phenomena observed in these solid solutions is the instability of the ferroelectric phase: Once the neighborhood of the transition temperature is reached, the transition disappears upon subsequent cooling. A hypothesis for this instability is offered in terms of a two-state configuration-coordinate diagram.

I. INTRODUCTION

Recently some of the solid solutions $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ were found to be ferroelectric.¹ This is the first example of ferroelectricity (FE) in zinc-blende-based systems. The experimental evidence for such a conclusion was the behavior of the dielectric constant as a function of temperature and the observation of the hysteresis loop. Further evidence for ferroelectricity in these solid solutions was given by x-ray diffraction^{2,3} and by birefringence measurements.⁴ The x-ray-diffraction measurements provide an unambiguous proof of a phase transition through the determination of the structures of the two phases: The measurements show that the high-temperature phase is cubic with the zinc-blende structure and that the low-temperature phase is rhombohedral, as evidenced by a slight distortion of the cubic cell. The analysis of the dielectric results shows that the transition is of second order but not sharp.

In this work we: (i) present new data concerning the ferroelectric properties of the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ solid solutions; (ii) show that different quantities, such as the polarization, the specific heat, and the birefringence, can be related to one another as observed in other ferroelectrics; (iii) give measurements of the dielectric constant at different frequencies; and (iv) discuss the instability of the ferroelectricity in terms of a configuration-coordinate model. A central observation here is that unlike common ferroelectrics, this system seems to have two distinct phases: one that does not exhibit FE at any temperature, and one that does (below a transition temperature). Indeed, while as-grown samples usually exhibit ferroelectricity, samples heated just above the transition temperature often lack FE once cooled again. High-temperature-annealed samples show recovery of ferroelectricity. This type of behavior was also noted in Ref. 5. The clear-cut evidence that the loss of FE is not due to reorganization of ferroelectric domains is the determination of the structure by x-ray diffraction: After heating, these samples have a cubic structure at room temperature.

We will suggest a hypothesis for this type of behavior in terms of a two-state model. Its clarification is a subject for future studies.

II. EXPERIMENTAL DETAILS

Single $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}$ crystals were grown by the modified Bridgman technique as described in a previous article.⁶ We do not use any procedure to polarize the samples. The samples were cut from the grown crystal, polished, and kept in darkness for some days before beginning the measurements. When needed, metal contacts were prepared by electroless deposition of gold from a gold chloride solution, as described in Ref. 7. The HAuCl_4 crystals were diluted in just enough water to make a slightly viscous solution. This solution was used to paint the contacts, which were then left to dry and form for 72 h at ambient conditions. Prior to applying the gold chloride solution to the sample, the contact surfaces were mechanically polished and then etched in a 5% Br in methanol solution for about 30 s. This procedure yielded low-resistance contacts with essentially linear I - V curves. All the equipment used to heat or cool the samples is standard and we shall only give a brief description of the methods for each kind of measurement.

III. POLARIZATION VERSUS TEMPERATURE

Two well-known techniques were used to measure the polarization: the hysteresis loop method and the method of integration of the pyroelectric coefficient proposed by Chynoweth⁸ to which we have applied a new analysis. The first method can be used at low temperatures, but is of limited use at high temperatures because the samples are conductive ($\sigma \sim 10^{-3} \Omega^{-1} \text{cm}^{-1}$ at room temperature for $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}$). In the Chynoweth method the large face of a flat sample (direction [111]) is illuminated by a modulated light from a Ne-He laser beam. The direction of the polarization, as deduced from previous measurements,¹ was $\langle 111 \rangle$. The current produced in the samples can have

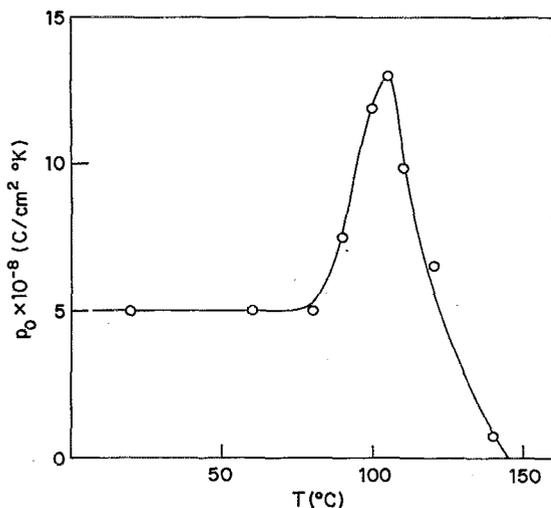


FIG. 1. Pyroelectric coefficient p_0 vs temperature T .

three origins: the photoelectric effect, the thermoelectric effect, and the pyroelectric effect. The photoelectric current is eliminated by covering the illuminated gold electrode with graphite. At the same time, we are assured that all the light is absorbed and heats the sample. Appendix A^{9,10} describes the method that allows the distinction and separation of the two other contributions: thermoelectric and pyroelectric currents.

Figure 1 shows the temperature dependence of the pyroelectric coefficient measured on a sample in which the pyroelectric current is much larger than the thermoelectric current. The pyroelectric coefficient p_0 is deduced from expression (A5) in Appendix A, using the values of the heat capacity obtained independently (see Sec. VII below). Note the peak in $p_0(T)$ at $T=105^\circ\text{C}$. Figure 2 shows the polarization P vs T , as determined from the two methods: directly from the hysteresis loop and from integration of the pyroelectric coefficient $p_0(T)$ (with the reasonable as-

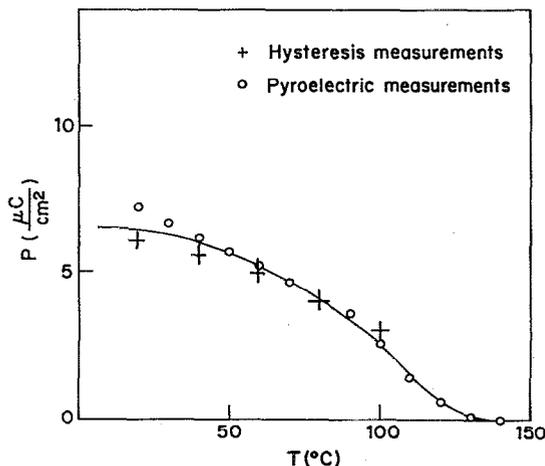


FIG. 2. Temperature dependence of polarization P as obtained from two different techniques: hysteresis loop and integration of the pyroelectric coefficient.

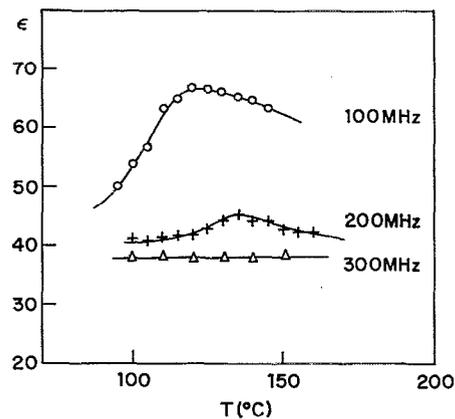


FIG. 3. Temperature dependence of dielectric constant ϵ at different frequencies. Note that at 300 MHz the transition is no longer visible.

sumption that $p=0$ at $T=140^\circ\text{C}$; see Fig. 1). There is a good agreement between the two curves when both methods are used at $T < 100^\circ\text{C}$. The curve deduced from p_0 shows clearly that the transition is diffuse, rather than sharp, in accordance with the measurements of the dielectric constant.¹

IV. DIELECTRIC MEASUREMENTS AT DIFFERENT FREQUENCIES

In Ref. 1, measurements of the dielectric constant ϵ have been presented at a single frequency of 100 MHz. In the present investigation, the measurements are extended up to 300 MHz. We used a Hewlett-Packard model 8508A vector voltmeter associated with a reflectometer. The experimental setup is computerized. Figure 3 shows $\epsilon(T)$ at three frequencies (100, 200, and 300 MHz) for T around the transition temperature. The frequency has a strong effect on the amplitude of ϵ : It decreases as the frequency increases. At 300 MHz, the transition is no longer visible. At the same time, the maximum in $\epsilon(T)$ is shifted to a higher temperature when the frequency increases. These observations are similar to those noted in other ferroelectric solid solutions such as $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ and disordered compounds such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ and $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$.¹¹

In polar dielectrics, the dielectric constant at a fixed temperature decreases when the frequency ω increases. The absolute value of the slope $d\epsilon/d\omega$ is maximum for a frequency equal to the inverse of a characteristic time τ . In an ideal ferroelectric this time is the relaxation time associated with the polarization dynamics,¹² but for a diffuse transition it has been shown¹³ that here is a distribution of relaxation times and τ is a mean value of the distribution. In our case, a strong decrease of ϵ appears between 100 and 300 MHz (Fig. 3). Taking the slope of ϵ vs ω in Fig. 3 at this frequency range we find that τ is between $(2\omega \times 10^8)^{-1}$ and $(6\omega \times 10^8)^{-1}$, i.e., $\tau \sim 10^{-9}$ s. This relatively high relaxation time is indicative of an order-disorder transition.¹²

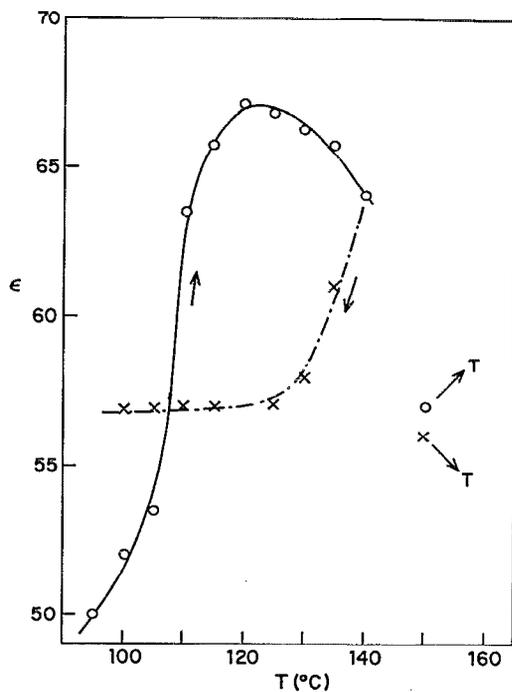


FIG. 4. Dielectric constant ϵ as a function of temperature T at 100 MHz on heating (\circ) and cooling (\times) the sample. During cooling, one does not observe the anomaly in ϵ .

The occurrence of a maximum in $\epsilon(T)$ (Fig. 3) depends on the thermal history of the sample. Figure 4 shows $\epsilon(T)$ for increasing T (\circ) and for decreasing T (\times) at 100 MHz. In the cooling cycle, we did not observe the maximum in ϵ which appeared on heating. This is one example of disappearance of ferroelectricity in our samples. The behavior of Fig. 4 signals the disappearance of ferroelectricity rather than domain redistribution, since even if there was a new domain distribution, we should have observed a peak in $\epsilon(T)$. This point is developed in Appendix B.¹⁴ We conclude that the absence of a transition once the sample had been heated to T_c does not result from domain reorientation.

V. X-RAY DIFFRACTION

Powder-x-ray-diffraction measurements were conducted both below and above the ferroelectric transition temperature. The diffraction peaks of the zinc-blende structure are split below the transition temperature, and become single peaks above this temperature. This is illustrated in Fig. 5. After cooling again, the splitting is usually not reproduced. The splitting is consistent with a rhombohedral distortion with an angle of 89.4 ± 0.1 . Marbeuf *et al.*³ have also found a rhombohedral distortion, with an angle of 89.94° . The splitting was resolved in the experimental spectra for all peaks with indices greater than [311].

VI. BIREFRINGENCE VERSUS TEMPERATURE

The birefringence of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ was measured¹⁵ at a wavelength of $10.6 \mu\text{m}$ for $x=0.04$ and 0.10 . Figure 6

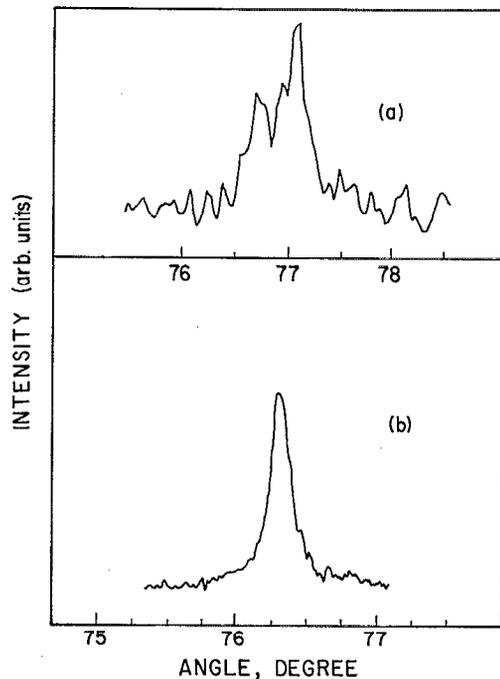


FIG. 5. Powder-x-ray-diffraction line [511] of $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}$ at 35°C (a) before heating and (b) after quenching from 160°C .

shows the variation of Δn , the difference between the index of refraction parallel to the polarization direction n_e , and perpendicular to the polarization direction n_o for these two samples. The disappearance of the birefringence above T_c is evident. Figure 7 displays the temperature coefficient $(dn/dT)/n$ for the two refraction indices. Note that the maximum in $(dn/dT)/n$ is due to the diffusiveness of the transition: If the transition had been sharp, a divergence would have been observed.

As was the case for the dielectric constant, polarization measurements and the split x-ray-diffraction peak, the birefringence too disappeared during the second heating of the sample. We have been able to restore the ferroelectric state in some samples by an annealing procedure at about 700°C under a Te atmosphere (to preserve stoichiometry).

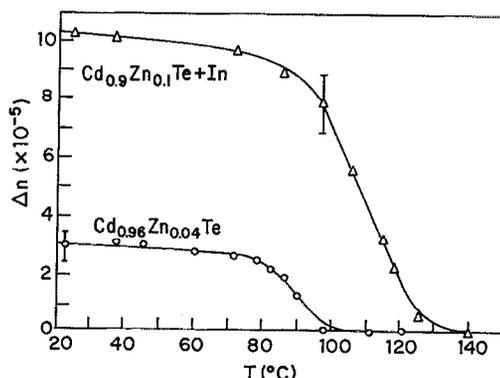


FIG. 6. Birefringence Δn vs temperature T for two samples: $x=0.04$ and $x=0.1$.

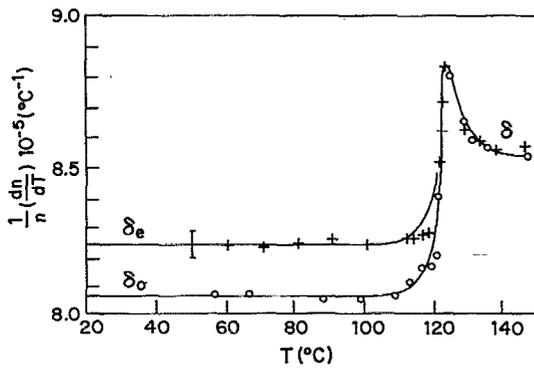


FIG. 7. Temperature dependence of $\delta = (dn/dT)/n$ for the ordinary (δ_o) and extraordinary (δ_e) refraction indices for the $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}$ sample.

We still do not control the procedure to our satisfaction, and research on a more reproducible and reversible procedure is continuing.

We next consider the dependence of Δn on polarization. Two cases are possible¹⁶ depending on whether the high-temperature phase is piezoelectric: (i) If the high-temperature (paraelectric) phase is nonpiezoelectric then $\Delta n \sim P^2$; here, (dn/dT) can exhibit either a jump (if the transition is sharp) or a smooth variation (if the transition is diffuse); (ii) If the high-temperature (paraelectric) phase is piezoelectric $\Delta n \sim P$; here (dn/dT) exhibits either a divergence at T_c (if the transition is sharp), or a maximum (if the transition is diffuse).

In our case, the high-temperature phase has the cubic zinc-blende structure (as checked by x-ray diffraction) which is piezoelectric. We find a maximum in (dn/dT) (Fig. 7), hence, the transition is of second-order type, but diffuse. The proportionality of Δn with P is shown in Fig. 8. We get a straight line for temperature above 80 °C. The reason for the deviation from the straight line at lower temperatures (Fig. 8) is not clear.

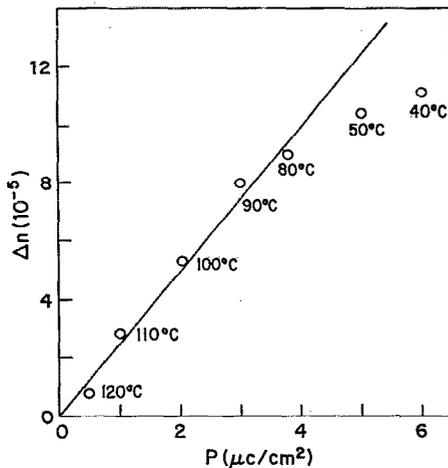


FIG. 8. Birefringence n vs polarization P curve showing the linearly dependent region. The points for $T < 60$ °C are not on the straight line.

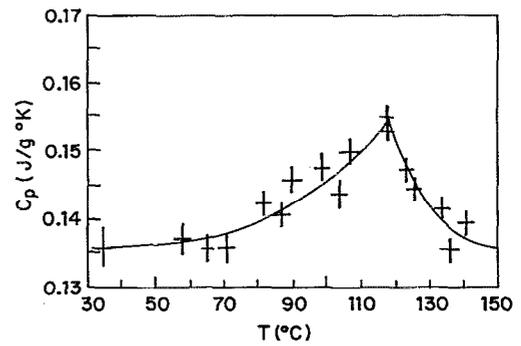


FIG. 9. Variation of the specific heat C_p with temperature T .

VII. SPECIFIC HEAT VERSUS TEMPERATURE

The specific heat was measured as follows: We took a small $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}$ sample ($1.1 \times 1.6 \times 1 \text{ mm}^3$) and covered its face with graphite. This face was exposed to a CO_2 laser beam. The intensity was varied with time as a step function: $I=0$ for $t < 0$; $I=\text{const}$ for $t > 0$. If the heating is uniform and there are no losses, the temperature increase should be linear with time with the slope $(dT/dt) = I/(mC_p)$, where C_p is the specific heat at constant pressure. When there are heat losses, the slope decreases with time, but it is still a good approximation to suppose that at $t=0$ the slope is given by the above expression. $C_p(T)$ was deduced from the determination of $dT/dt(t=0)$. Analysis of the problem, taking into account that the heating in the sample is not uniform, shows that the error is about 5%.¹⁴ Hence, the method we used has the advantage of simplicity but it is not very precise.

In Fig. 9, the variation of C_p with the temperature is shown. The behavior is consistent with a diffuse transition. The dependence expected from a sharp second-order transition would have been either a step (mean-field transition) or a divergence (critical behavior).

VIII. RELATION BETWEEN SPECIFIC HEAT AND POLARIZATION

In ferroelectrics, the Landau–Devonshire (LD) theory¹⁶ gives a good phenomenological analysis of the experimental observations for sharp, second-order transitions. In our case, the transition is diffuse so a straightforward application of the LD theory is not possible. However, as was previously shown,¹ outside the transition region our results are in accordance with a mean-field second-order phase transition (as given by the LD theory): $P^2 \propto (T_c - T)$ and the ratio of the slopes $(d\epsilon^{-1}/dT)$ above and below T_c is very nearly 2.

From the LD expansion¹⁶ of the free energy

$$G = G_0 + \frac{1}{2}\beta(T - T_c)P^2 + \gamma P^4, \quad (1)$$

it is possible to show that the heat capacity is related to the polarization by

$$C_p - C_{p_0} = -T\beta P \frac{dP}{dT}. \quad (2)$$

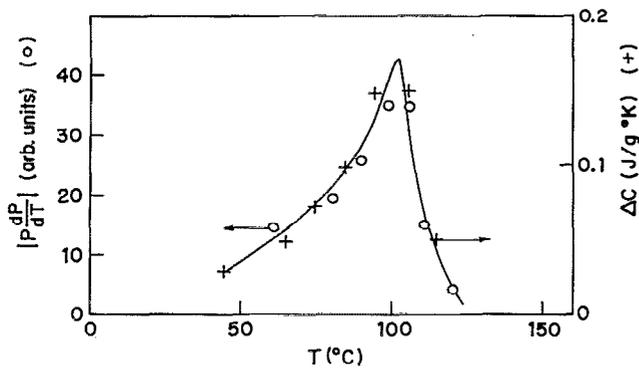


FIG. 10. Excess specific heat ΔC_p (crosses) and $|PdP/dT|$ (circles) vs temperature T mapped onto the same graph, showing the proportionality of the two quantities.

It has been noted¹⁷ that the relation (2) should also be valid for diffuse transitions. We shall thus apply Eq. (2) to our case.

In Fig. 10 we plotted $C_p - C_{p0}$ (from Fig. 9) and $|P(dP/dT)|$ (from Fig. 2) making: (a) a shift of 15 °C downward for the C_p data, and (b) an appropriate adjustment of the scales. This way, we force the two curves to coincide (but only for $T > 60$ °C) as indicated by Eq. (2). The shift of 15 °C is probably due partly to small differences in the composition of the samples, and partly due to a systematic error in the measurements of the temperature. From this fit we can calculate the quantity βT_c and compare it with the value of the Curie constant equal to $1/\beta$. We found $(\beta T_c)^{-1} \approx 2$ compared with $C/T_c = 2.11$ deduced from the dielectric measurements for the 10% sample. The agreement is very good (probably accidental). Thus formula (2), which links the Curie constant, the specific heat, and the polarization, is verified in this diffuse transition.

IX. DISCUSSION

The measurements presented in this article, i.e., polarization, specific heat, birefringence, dielectric constant, and the x-ray diffraction give a picture of the ferroelectricity in the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ solid solutions. The transition is a second-order diffuse transition. The polarization at room temperature is about $5 \mu\text{C}/\text{cm}^2$, this is comparable to the values found in "classical" ferroelectrics such as triglycine sulfate or potassium dihydrogen phosphate. The relations $\Delta n \sim P$ and $C_p \sim |PdP/dT|$ are observed although the transition is not sharp. Macroscopically, one can say that these solid solutions behave as regular ferroelectrics. However, it is necessary to explain why a small amount of Zn gives such a high transition temperature. Only 4% of zinc gives $T_c \approx 90$ °C (363 K). This can be compared with an analogous system $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$ for which $x=10\%$ corresponds only to $T_c \approx 220$ K.¹⁸

A central hallmark of the ferroelectricity in this system is its dependence on the thermal history. For example, while as-grown samples exhibit a polarization decay (Fig. 2) and loss of birefringence (Fig. 6) at $T > T_c$, a low-

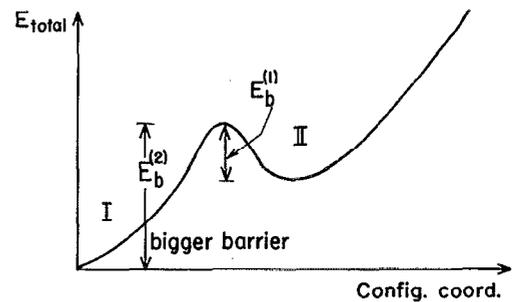


FIG. 11. Schematic configuration-coordinate diagram illustrating the proposed two-state system.

frequency dielectric peak (Fig. 3) and a specific-heat peak (Fig. 9) at T_c , and a splitting of the zinc-blende diffraction peak below T_c (Fig. 5), once the neighborhood of the transition temperature is reached, most of the time, subsequent cooling leads to the disappearance of these effects. Furthermore, heating again the samples that have reached T_c leads to a weak (or absent) ferroelectricity. The ferroelectric behavior can be restored in some samples by a high-temperature (~ 700 °C) anneal in a Te atmosphere. These effects are not understood at the present time. It is conceivable, however, that this system could consist of two distinct thermodynamic states: one (state I) that does not exhibit ferroelectricity at any temperature and the other (state II) that is ferroelectric below T_c and paraelectric above it. Denote the energy difference of these two states by Δ . The system in state I can correspond structurally to an ordinary zinc-blende solid solution that is nonferroelectric, while the system in state II could correspond to a statically deformed lattice whose lower overall symmetry (see the x-ray data) permits ferroelectricity. The two states can be thought of as two distinct minima in a configuration-coordinate diagram. These minima can be separated by activation barriers $E_b^{(1)}$ and $E_b^{(2)}$ as illustrated schematically in Fig. 11. This qualitative model can then be used to speculate on the nature of the unstable ferroelectricity in CdZnTe, as follows: Samples whose thermal history or growth conditions placed them in state II (e.g., as-grown samples) exhibit ferroelectricity. Only a fraction $N_0 e^{-\Delta/kT}$ of all atoms are trapped in this state. However, when heated sufficiently to overcome the barrier $E_b^{(1)}$, part of the sample transforms into the nonferroelectric state I. If the energy of state I is deeper (by Δ) than that of state II, such thermal treatments at $T \gtrsim T_c$ will result in "trapping" of more particles in the deeper minima, hence reduce the ferroelectricity. These particles can be released only if the sample is annealed at a temperature $T \gg T_c$ to overcome the larger barrier $E_b^{(2)}$.

To search for a microscopic model that could result in such a situation, we have studied theoretically¹⁹ off-center atomic displacements in ordinary zinc-blende semiconductors. A "supercell," consisting of four cations and four anions, originally placed at the zinc-blende atomic positions was constructed. The total energy was calculated in the local density approximation,²⁰ as implemented by the

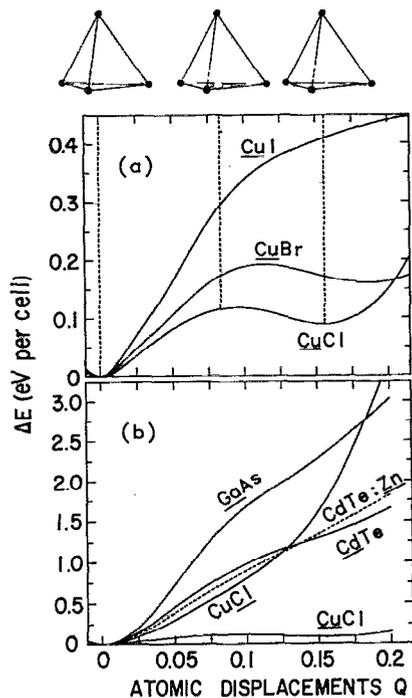


FIG. 12. Results of first-principles LAPW total energy calculations illustrating the off-center behavior in some zinc-blende semiconductors.

linear augmented plane wave (LAPW) method.²¹ A single cation atom was then displaced from the tetrahedral site along the three-fold axis of the tetrahedron (the [111] direction), resulting in a C_{3v} symmetry (see the x-ray studies). The total energy versus displacement is reproduced in Fig. 12. We see that for a system with active cation d orbitals such as CuCl, there exists indeed a secondary, off-center minimum, as envisioned in Fig. 11. The details of the microscopic mechanism leading to this instability—a displacement-induced coupling between the occupied d bands and the empty s conduction bands (the “pseudo-Jahn-Teller” effect)—will be discussed in a future publication.¹⁹

As pointed out by Bersuker *et al.*,²² the t_2 -type normal-mode displacements in XY_4 tetrahedral systems induce a dipole. In state II there are four local-equilibrium configurations corresponding to the four bond directions. In each minima, the dipole coincides with the direction of the bond. At high temperatures (as long as the system is in state II) the system jumps dynamically between these minima through tunneling. The observed net dipole will then depend on temperature and tunneling rate. In the absence of correlation between the tetrahedra, the system as a whole will be unpolarized. As the temperature is lowered, the dipole correlation is enhanced and a net polarization will appear as a result of an order-disorder transition. Note that the ferroelectricity in such a system is metastable ferroelectricity, since the true ground state has the nonferroelectric zinc-blende structure.

Since the off-center displacement found in CuCl derives from a metal d - s coupling, it is expected to be weaker

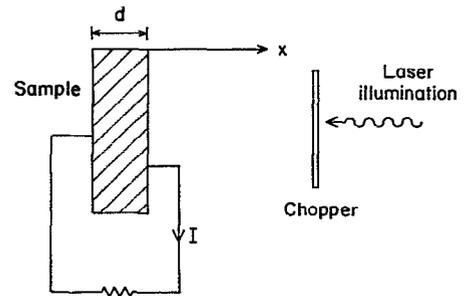


FIG. 13. Schema of the pyroelectric and thermoelectric measurements.

the deeper bound the metal d bands are. While photoemission studies show that CuCl has d bands near the top of its valence band,²³ II-VI compounds have considerably deeper d bands,²⁴ hence less d - s coupling. A calculation analogous to that shown in Fig. 12 for CuCl was performed for a $ZnCd_3Te_4$ supercell (25% Zn). This calculation reveals strong anharmonicities, but no distinct secondary minimum. It is possible that yet lower-symmetry configurations akin to the disordered alloy environment could lead to a metastable minimum. Hence, while the conceptual model envisioned in Fig. 11 seems applicable to I_B -VII systems, direct evidence for its applicability to II-VI systems is lacking. Nevertheless, this model suggests a direction for future experimental research: characterize the preparation conditions, thermal treatment, or photoinduced effects that maximize the population of state II, hence the amplitude of the FE. Conceivably, samples in state I and state II could differ in their vibrational properties (as was seen by Livescu and Brafman²⁵ in CuCl) as well as in splitting of absorption bands, polarization, birefringence, etc. Furthermore, if the dipoles in this system are induced by the Cd-Zn size difference which leads to off-center displacements, a similar effect should be seen in other size-mismatched alloys, e.g., GaP/InP or GaAs/InAs. These experimental studies should be pursued.

ACKNOWLEDGMENTS

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APPENDIX A

The experimental situation for the measurement of the pyroelectric current is shown in Fig. 13. A slab (thickness d) is illuminated by a modulated laser beam [intensity $W_1 + W_0 \exp(j\omega t)$]. The thermal contact of the second face with the holder is characterized by a relaxation time τ_1 . If other dimensions are larger than the thickness, the excess temperature will depend only on x and t . In the steady-state regime⁹ T is equal to

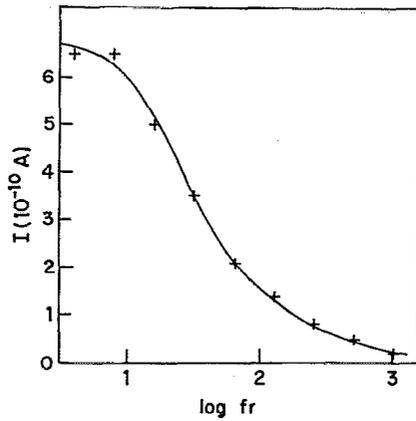


FIG. 14. Current I vs $\log f$ for a CdTe sample. The line is a fit following Eq. (A3).

$$\Delta T(x,t) = \frac{W_0}{C_p \rho d} \left[\frac{\tau_1}{1 + \gamma \omega \tau_1} + 2 \sum_{n=1}^{\infty} \cos\left(\frac{n\pi x}{d}\right) \times \frac{\tau/n^2}{1 + \gamma \omega \tau/n^2} \right] e^{j\omega t}. \quad (\text{A1})$$

In Eq. (A1), a constant term proportional to W_1 was not included since only the time-dependent part of ΔT was of interest. C is the heat capacity, ρ is the sample density, τ is equal to $d^2/\pi D$ with D being the thermal diffusivity.

The thermoelectric current is equal to

$$I_{\text{th}} = (K/R) [\Delta T(x=0) - \Delta T(x=d)], \quad (\text{A2})$$

where K is the thermoelectric power and R is the total resistance of the circuit. One obtains

$$I_{\text{th}} = \frac{4KW_0}{RC_p \rho d} \sum_{n=1,3,5} \frac{\tau/n^2}{1 + \gamma \omega \tau/n^2}. \quad (\text{A3})$$

To verify the validity of this expression a sample of CdTe ($4 \times 5 \times 0.8 \text{ mm}^3$) was prepared, and I_{th} was measured as a function of frequency. The experimental results are indicated in Fig. 14 by the points and the line is the result of the fit using Eq. (A3). It suffices to take two terms ($n=1, n=3$) in the sum. The fit is excellent and this gives confidence in the validity of expression (A1). The value of K deduced from the fit and all the other known quantities is $250 \mu\text{V/K}$. It compares well with the results of Kubalkova for a p -type sample with 10^{14} holes/cm³ as our CdTe sample.¹⁰ The pyroelectric current is given by

$$I_{\text{pyro}} = \frac{S}{d} \int_0^d \frac{\partial \Delta T}{\partial t}(x,t) dx, \quad (\text{A4})$$

where S is the sample surface (S being the illuminated surface) and p_0 is the pyroelectric coefficient. If T is small enough, p_0 can be taken constant through the sample. Using Eqs. (A1) and (A4) one has

$$I_{\text{pyro}} = \frac{S p_0 W_0}{C_p \rho d} \frac{\gamma \omega \tau_1}{1 + \gamma \omega \tau_1}. \quad (\text{A5})$$

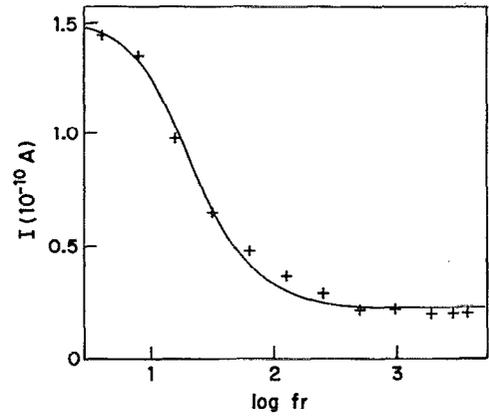


FIG. 15. Current I vs $\log f$ for a $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}$ sample, showing that for large frequencies the current goes toward a finite value. The line is a fit obtained using expressions (A3) and (A5).

In the case of simultaneous occurrence of both effects, the total current is the sum of the two contributions.

The absolute value I_{th} is characterized by a monotonic decrease when ω increases from zero to ∞ . There is a simple and clear-cut distinction between the two effects: A sample with a pyroelectric effect will give a finite value for the current at high frequencies.

In Fig. 15, a sample with the two contributions is shown. The results are fitted taking for the total current $I = I_{\text{th}} + I_{\text{pyro}}$. It appears that τ_1^{-1} is smaller than the lowest frequency and this means that the pyroelectric contribution (if it was alone or much larger than I_{th}) has no frequency dependence. As shown in Fig. 15 by the solid line, the fit is very good.

In the course of this work, three kinds of $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}$ samples were distinguished: (a) those with the two contributions not too different as in Fig. 15; (b) those with the pyroelectric current much larger than the thermoelectric current; as expected, the current is independent of ω ; (c) those with the thermoelectric current much larger than the pyroelectric one. The dependence of I on ω is similar to that shown in Fig. 14 for pure CdTe. We think that these differences correspond to nonequivalent [111] directions.

It is interesting to note that in the case (c), the thermoelectric coefficient as a function of T exhibits a small anomaly at the transition temperature, near 100°C .

APPENDIX B

The Landau–Devonshire expansion of the free energy of a ferroelectric crystal with a cubic paraelectric phase and a rhombohedral ferroelectric phase is

$$G = \frac{1}{2}A(P_x^2 + P_y^2 + P_z^2) + \frac{1}{4}B(P_x^4 + P_y^4 + P_z^4) + \frac{1}{2}C(P_x^2 P_y^2 + P_y^2 P_z^2 + P_z^2 P_x^2), \quad (\text{B1})$$

with $A = A_0(T - T_c)$ and $C > B$.

This last condition is necessary in order to insure that the rhombohedral ferroelectric phase will be the most stable.¹⁴ The components of the spontaneous polarization are deduced from the conditions

$$\frac{\partial G}{\partial P_x}=0, \quad \frac{\partial G}{\partial P_y}=0, \quad \frac{\partial G}{\partial P_z}=0,$$

or

$$\begin{aligned} AP_x + BP_x^3 + CP_x(P_y^2 + P_z^2) &= 0, \\ AP_y + BP_y^3 + CP_y(P_x^2 + P_z^2) &= 0, \\ AP_z + BP_z^3 + CP_z(P_x^2 + P_y^2) &= 0. \end{aligned} \quad (\text{B2})$$

The rhombohedral solution is $P_x = P_y = P_z = P_0$ with P_0 given by

$$A + (B + 2C)P_0^2 = 0. \quad (\text{B3})$$

From Eq. (B3), one sees that P_0 varies as $(T_c - T)^{1/2}$.

Now we apply electric field (E_x, E_y, E_z) . From $dG/dP_x + E_x$ (and similar expressions for P_y and P_z), one finds (for $T < T_c$)

$$\begin{aligned} E_x &= 2BP_0^2\delta P_x + 2CP_0^2\delta P_y + 2CP_0^2\delta P_z, \\ E_y &= 2BP_0^2\delta P_y + 2CP_0^2\delta P_x + 2CP_0^2\delta P_z, \\ E_z &= 2BP_0^2\delta P_z + 2CP_0^2\delta P_x + 2CP_0^2\delta P_y, \end{aligned} \quad (\text{B4})$$

with

$$P_x = P_0 + \delta P_x, \quad P_y = P_0 + \delta P_y, \quad P_z = P_0 + \delta P_z.$$

The components of the susceptibility tensor χ_{ij} are $\delta P_i/E_j$. From Eq. (B4) it is easy to see that all the $\chi_{i,j}$'s are proportional to P_0^{-2} ; therefore, they all diverge at T_c . Above T_c χ is equal to $A_0^{-1}(T - T_c)^{-1}$. Thus, we conclude that when measuring the dielectric constant by applying an electric field, one gets a divergence whatever its direction is. In our case, it means that an anomaly must always be observed, independently of the domain distribution.

The slope $d\epsilon^{-1}/dT$ is dependent on the chosen direction. Only if the field is parallel to the spontaneous polarization the ratio of the slopes below and above T_c is equal

to 2. This was observed in our samples for the [111] direction. This is a further evidence that this direction is that of the polarization.

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