Fig. 9. Variation of $(dE/dP)_0$ versus x

field" for each composition subjected to both the compression and decompression phase. These diagrams confirm that composition with $x = 0.05$ and $x = 0.06$ are antiferroelectric and metastable ferroelectric after polarization.

The compositions corresponding to $x > 0.06$ are ferroelectric since the two transitions $F \rightarrow AF$ and $AF \rightarrow F$, in the absence of action of the electric field, call for a positive pressure.

The transition pressure varies linearly with the electric field. The transition slope $F \rightarrow AF$, at increasing pressure, allows $(\delta E/\delta p)_0$ to be determined for this transition (Fig. 9).

The influence of pressure and composition on the $F \rightarrow AF$ transition is given in Fig. 5. In extrapolating the straight lines $p = f(E)$ representing the $AF \rightarrow F$ transition in the "pressure-electric field" diagrams, it is possible to derive the pressure of the $AF \rightarrow F$ transition in the coercive field for each composition (Fig. 8). The transition pressure is assumed to be below constant for values of the electric field that are below those of the coercive field. One obtains the entire phase diagram "pressure-composition" shown in Fig. 5.

3. Thermodynamics of the Pressure Enforced $F \rightarrow AF$ Transition and Introduction of New Piezoelectric Coefficients

Neglecting any variation in temperature the general equations can be written with only two thermodynamic variables: the electric field E [V/m] and the hydrostatic stress p [N/m²] (p is considered positive for compression). The standard piezoelectric equa-

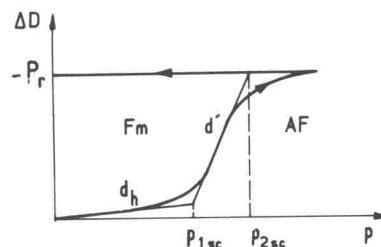


Fig. 10

tions $dD = \epsilon dE - d_h dp$ and $dV/V = -Sdp + d_h \cdot dE$ can be applied to poled ferroelectrics, metastable or not, only in the case of linear and reversible phenomena. The following symbols are used

dD = variation of dielectric displacement [C/m²],

dV/V = relative volume variation (dimensionless),

S = elastic compliance at constant electric field [m²/N],

$d_h = -(\delta D/\delta p)_E$ = hydrostatic piezoelectric coefficient at constant electric field [C/N],

$\epsilon = (\delta D/\delta E)_p$ = dielectric permittivity at constant pressure [F/m].

These relations are valid if the pressure is lower than the pressure p_1 for which the transition takes place.

During the transition process, i.e. between the pressures p_1 and p_2 (p_2 = pressure at the end of the transition), it is possible to define three new coefficients d' , ϵ' , g' characterizing the $F \rightarrow AF$ phase transition. The piezoelectric coefficients $d' = -(\delta D/\delta p)_E$ is the slope of the linear ferroelectric-antiferroelectric phase boundary in the diagram "short circuit charges versus hydrostatic stress" (Fig. 10). The total change of dielectric displacement during the compression results from the liberation of the remanent charge of polarization P_r . From the following equations

$$D = \int_0^D dD = -d' \int_{p_{1sc}}^{p_{2sc}} dp = -P_r$$

and

$$p_{2sc} - p_{1sc} = \Delta p_{sc} = \frac{P_r}{d'}$$

we find easily

$$d' = \frac{P_r}{\Delta p_{sc}}$$

The permittivity ϵ' at constant pressure during the transition, i.e. $\epsilon' = (\delta D/\delta E)_p$, may be defined from the hysteresis loop $P = f(E)$ of samples previously in the

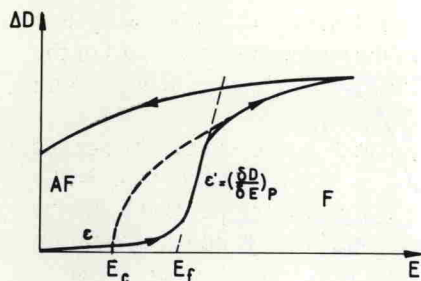


Fig. 11

antiferroelectric state [1]. The quantity ϵ' denotes the slope of the linear AF \rightarrow F phase boundary in the diagram "charge density versus electric field" (for the first cycle), see Fig. 11. We assume that ϵ' has the same value for an F \rightarrow AF transition.

The piezoelectric coefficient $g' = (\delta E / \delta p)_D$ may be derived by equations similar to the standard piezoelectric equations with new parameters defined for the F \rightarrow AF transition, namely

$$dD' = \epsilon' dE - d' dp \quad (1)$$

$$dV'/V = -S' dp + d' dE \quad (2)$$

$$d' = (1/V) (\delta V' / \delta E)_p \quad \text{and} \quad -S' = (1/V) (\delta V' / \delta p)_E,$$

where S' is the slope of the F \rightarrow AF phase boundary in the diagram "volume strain versus hydrostatic pressure". From (1) it follows $(\delta E / \delta p)_D = d' / \epsilon'$. at constant dielectric displacement. For the entire transition taking into account the relative volume change $\Delta V'/V$ and the change of the electric field $\Delta E = P_r / \epsilon'$ it results the piezoelectric coefficient $d' = (\Delta V'/V) / (P_r / \epsilon') = \epsilon' g'$, where $g' = (\Delta V'/V) / P_r = d' / \epsilon'$.

As a final result we find the same relation as for the standard piezoelectric coefficients g_h and d_h , namely $g_h = d_h / \epsilon$. We also have

$$-S' = (1/V) (\delta V' / \delta p)_E = -(\Delta V'/V) / \Delta p_{sc}$$

$$= -(\Delta V'/V) / (P_r / d')$$

$$S' = d' g'$$

and (2) becomes $dV'/V = -d' g' dp + d' dE = g' dD'$.

We may remark that in the standard piezoelectric equations the electromechanical coupling factor k is given by $k^2 = d_h g_h / S$. During the transition process the electromechanical factor k is equal to unity: $k'^2 = d' g' / S = 1$. This result, previously mentioned [6], is also obtained by setting the Gibbs free energy equal for states AF and F, i.e.

$$\Delta E \cdot \Delta D' = (\Delta V'/V) \Delta p.$$

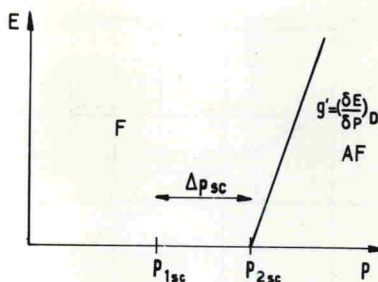


Fig. 12

This relation shows that the mechanical and electrical energies exchanged during the phase transition are perfectly coupled.

The coefficient g' denotes the slope of the F \rightarrow AF linear phase boundary in the phase diagram: "electric field versus hydrostatic pressure" (Fig. 12).

(1) and (2) describe only the variations which occur during the phase transition. These changes must be added to the standard piezoelectric effect between p_1 and p_2 . So, for each state of the ceramic we have the following equations

Ferroelectric phase

$$p < p_1 \quad \left| \begin{array}{l} dD = \epsilon dE - d_h dp \\ dV/V = d_h dE - S dp \end{array} \right.$$

During the phase transition:

$$p_1 < p < p_2 \quad \left| \begin{array}{l} dD = \epsilon dE - d_h dp + \epsilon' dE - d' dp \\ dV/V = d_h dE - S dp + d' dE - d' g' dp \end{array} \right.$$

Antiferroelectric phase:

$$p > p_2 \quad \left| \begin{array}{l} dD = \epsilon dE \\ dV/V = -S dp. \end{array} \right.$$

Let us consider now the particular case of an hydrostatic stress applied to an open-circuit ceramic:

For $p < p_1$ we find $dD = 0$ and therefore $dE/dp = d_h / \epsilon = g_h$ and in the region $p_1 < p < p_2$ for $dD = 0$ we obtain $dE/dp = d' / \epsilon' = g'$.

Assuming that we have again $\epsilon dE - d_h dp = 0$ we note that $dD' = \epsilon' dE - d' dp = 0$ involves $dV'/V = g' dD' = 0$. The F \rightarrow AF phase transition is completely clamped by the electric field. The deformation $dV'/V = -S dp + d_h dE$ is only due to the standard piezoelectric effect. Near pressure p_1 there is no transition effect, and we have $g_h = g' = d_h / \epsilon = d' / \epsilon'$. Therefore the slope of the F \rightarrow AF linear phase boundary in the diagram "electric field versus hydrostatic pressure" is equal to the standard piezoelectric coefficient g_h .