

specific heat measurement [Phys. Rev. 167, 504 (1968)]; it may be noted in addition that no reported measurement of the spontaneous polarization shows a value of  $P/P_s$  at the transition temperature less than about 0.2.

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## GADOLINIUM MOLYBDATE, A NEW TYPE OF FERROELECTRIC CRYSTAL\*

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(Received 11 July 1968)

Ferroelectric properties in gadolinium molybdate are shown to originate from a new mechanism completely different from that in conventional ferroelectric materials. In this crystal the spontaneous polarization results from an elastic instability which gives rise to a spontaneous strain in the original piezoelectric paraelectric phase. The dielectric permittivity of the clamped crystal ( $\epsilon_{33}^x$ ) is low and independent of temperature, while the elastic constant ( $c_{66}^E$ ) shows a strong temperature dependence with a marked anomaly at the Curie point.

Gadolinium molybdate,  $Gd_2(MoO_4)_3$ , has been shown by Borchardt and Bierstedt<sup>1</sup> to be ferroelectric at temperatures below 159°C, and recent more extensive measurements by Cummins<sup>2</sup> have confirmed this finding. These new data, however, show conclusively that the molybdate is not a conventional ferroelectric, but that the dielectric properties are essentially normal, and that the spontaneous polarization is the consequence of an elastic instability giving rise to a spontaneous strain in a piezoelectric structure. The evidence in support of this contention may be briefly summarized as follows.

Gadolinium molybdate is of tetragonal point symmetry  $42m$  above  $T_c$  which is 159°C. The ferroelectric phase is orthorhombic, the polar axis along  $c$ , the Aizu<sup>3</sup> class  $F\bar{4}2m(1)D\bar{4}$ . The argument for elastic instability can be illustrated by considering a very simple Gibbs free energy. Including only quadratic terms, for polarization along  $c$ , this may be written

$$\Delta G = \frac{1}{2}c_{66}^P x_6^2 - a_{36}P_3 x_6 + \frac{1}{2}\chi_{33}^x P_3^2, \quad (1)$$

where  $x_6$  is the shear deformation about  $c$ ,  $P_3$  is the polarization along  $c$ ,  $c_{66}^P$  is the elastic constant at constant  $P$ ,  $a_{36}$  is the piezoelectric constant, and  $\chi_{33}^x$  is the dielectric inverse susceptibility at constant strain. The expression is essentially similar to that for potassium dihydrogen phosphate<sup>4</sup> which has the same prototype symmetry.

From (1),

$$\partial \Delta G / \partial x_6 = -X_6 = c_{66}^P x_6 - a_{36}P_3, \quad (2)$$

$$\partial \Delta G / \partial P_3 = E_3 = -a_{36}x_6 + \chi_{33}^x P_3, \quad (3)$$

where  $X_6$  is the shear stress about  $c$  and  $E_3$  is the electric field in direction of  $c$ .

For a spontaneous state,  $X_6 = 0$ ,  $E_3 = 0$ , and substituting from (3) into (2), the condition for a non-zero deformation  $x_6 \neq 0$  is

$$c_{66}^P - a_{36}^2 / \chi_{33}^x = 0. \quad (4)$$

In conventional ferroelectricity,  $\chi_{33}^x$  is a decreasing function of  $T$ , passing through zero near

$T_C$ . The catastrophic increase of  $x_6$  and  $P_3$  is, of course, limited by the higher order terms in  $P_3$ , and the dielectric properties are necessarily nonlinear for temperatures close to  $T_C$ . It is clear, however, from (4) that the paraelectric phase would also become unstable if  $c_{66}^P$  decreased sufficiently. In this case, however, catastrophic collapse below  $T_C$  would be limited by the higher order elastic constants, and the dielectric properties apart from a spontaneous polarization could remain essentially linear.

That this second case is in fact the origin of the ferroelectric state in  $Gd_2(MoO_4)_3$  may be shown by two simple experiments:

(i) Measurements of  $\chi_{33}^X$ , or what is equivalent,  $\epsilon_c^X$  in the clamped condition, Fig. 1(a), show no change throughout the whole range of temperature from 25 to 180°C, and in particular give no indication of a Curie point at 159°C. The dielectric permittivity at constant and zero stress  $\epsilon_c^X$  [Fig. 1(b)], however, shows a weak anomaly at  $T_C$  which is, of course, a consequence of the piezoelectric coupling.

(ii) Measurements of  $c_{66}^E$ , or what is equivalent, the resonant frequency of a plate cut normal to the  $c$  axis and vibrating in a shear mode,

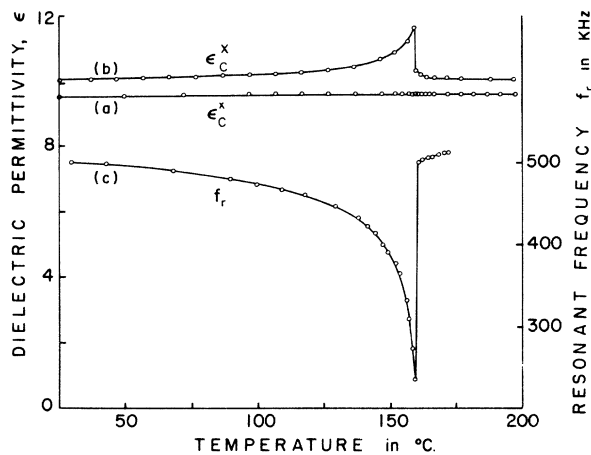


FIG. 1. Dielectric and elastic properties of a single crystal of gadolinium molybdate  $Gd_2(MoO_4)_3$ . (a) Dielectric permittivity  $\epsilon_c^X$  of the "inertia clamped" crystal as a function of temperature. The field is 20 V/cm along  $c$  direction and the frequency is 19 MHz. (b) Dielectric permittivity  $\epsilon_c^X$  of the "free" crystal as a function of temperature. The field is 20 V/cm along  $c$  direction and the frequency is 1 KHz. (c) Resonant frequency in KHz as a function of temperature of a crystal plate, cut perpendicular to  $c$  direction, vibrating in a shear mode.

show a strong anomaly at  $T_C$  [Fig. 1(c)]. Data from other cuts where the vibration also involves the  $c_{66}$  coefficient show that there is little difference between  $c_{66}^P$  and  $c_{66}^E$ , and that the elastic anomaly does not originate in a piezoelectric coupling.

It is obvious from Fig. 1(c) that in  $Gd_2(MoO_4)_3$  the elastic constant  $c_{66}$  does not become zero at  $T_C$ , i.e., the resonant frequency does not go to zero. The behavior would suggest that the phase transition at 159°C is first order; in this case, the instability occurs before condition (4) is satisfied, and the crystal goes discontinuously to a state of finite strain at  $T_C$ .

The nature of the dielectric hysteresis, particularly in the vicinity of  $T_C$ , and the very trivial effects of bias fields on the crystals also agree with the expected behavior of a linear but spontaneously polarized crystal.

It would appear that  $Gd_2(MoO_4)_3$  is the first member of a completely new class of ferroelectric crystals, in which spontaneous polarization and deformation occur without high permittivity, giving properties which may be exploited in device applications. Since the spontaneously deformed state is controlled by the higher order elastic constants, and the deformation is "labeled" by an easily measured polarization, materials of this type may contribute quite effectively to a better understanding of elastic properties at large strains, i.e., to higher order elastic constants.

In the context of this treatment, it may be pointed out that diammonium dicadmium sulphate  $(NH_4)_2Cd_2(SO_4)_5$  appears to have rather similar dielectric properties at constant stress. Since the cubic point group of the prototype has symmetry 32, the instability may again be elastic, and a measurement of  $\epsilon$  in the clamped condition for this crystal could be most interesting.

It is a pleasure to acknowledge very useful discussions with Dr. J. Fousek.

\*Work supported by the Advanced Electronic Devices Branch, Air Force Avionics Laboratory, Wright-Patterson Air Force Base, Ohio, and performed jointly in-house and under Contract No. F33615-67-C-1427. U. S. Air Force Office of Aerospace Research Project 7031 is the programming authority for this work.

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## CHARACTERISTIC STRUCTURAL PHASE TRANSITION IN PEROVSKITE-TYPE COMPOUNDS

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(Received 1 July 1968)

The tetragonal rotation of  $\text{TiO}_6$  octahedra in  $\text{SrTiO}_3$  and the trigonal rotation of  $\text{AlO}_6$  octahedra in  $\text{LaAlO}_3$  were measured by paramagnetic resonance below their respective phase transitions. The normalized rotation angles  $\alpha$  vary quantitatively in the same way as a function of reduced temperature. Thus  $\alpha$  is the order parameter in such transitions, which are characteristic for perovskite compounds.

Since the discovery of the phase transition from cubic to nonpolar tetragonal in  $\text{SrTiO}_3$  near  $100^\circ\text{K}$ ,<sup>1,2</sup> interest in the origin of this transition has not ceased. It was noted at the time<sup>2</sup> that such a transition may be typical for oxides crystallizing in the perovskite structure. Other possibilities have been proposed by Cowley<sup>3</sup> and Horner.<sup>4</sup> Both authors related the transition—in different ways—to the existence of the soft TO Cochran-Landauer mode at  $k=0$  present in this material.<sup>3</sup> In an effort to elucidate this phase transition we made a careful structural comparison with the one occurring in  $\text{LaAlO}_3$ , an oxide material, whose electric and magnetic properties are similar to normal oxides like  $\text{Al}_2\text{O}_3$  or  $\text{MgO}$ . Thus the transition in  $\text{LaAlO}_3$  would be characteristic for materials crystallizing with the  $\text{ABO}_3$  perovskite structure. In addition, transitions due to magnetic or electric interactions may be present as well ( $\text{PrAlO}_3$ ) and can even dominate ( $\text{BaTiO}_3$ ).

Geller and Bala<sup>5</sup> made an x-ray analysis of  $\text{LaAlO}_3$  and found it to be trigonal at  $300^\circ\text{K}$ , becoming cubic at  $\sim 720^\circ\text{K}$ . EPR powder measurements on  $\text{Gd}^{3+}$  revealed no other phase transition down to  $4.2^\circ\text{K}$ .<sup>6</sup> Similar measurements on single crystals confirmed this result, but it remained open at what temperature the cubic-to-trigonal transition occurred, and whether it was of first or second order.<sup>7</sup> We completed such an EPR study recently with a monodomain  $\text{LaAlO}_3$  crystal (containing 0.02%  $\text{Fe}^{3+}$  ions substitutional for  $\text{Al}^{3+}$ ) in the entire range from  $4.2$  to  $900^\circ\text{K}$ .<sup>8</sup> From the axial constant  $D(T)$  reproduced in Fig.

1(a), it is clear that the phase transition occurs at  $T_a = 800 \pm 10^\circ\text{K}$ , and is of second order.

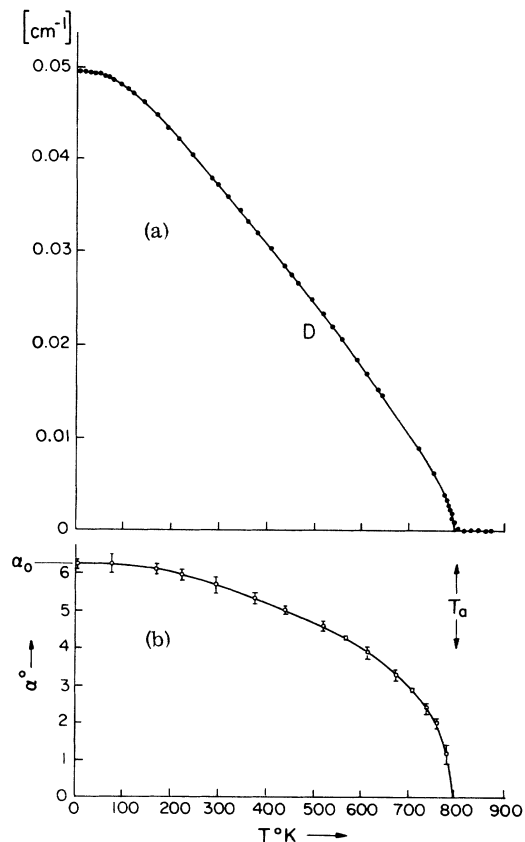


FIG. 1. (a) Axial splitting  $D$  of the  $\text{Fe}^{3+}$  EPR spectrum, and (b) trigonal rotation angle of the  $\text{AlO}_6$  octahedra in  $\text{LaAlO}_3$  as a function of temperature below  $T_a$ .