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Letters to the Editor

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Ferroelectricity of Dicalcium Strontium Propionate

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THE ferroelectric crystals known to date fall into two main groups. The first, containing the water-soluble Rochelle salt, potassium dihydrogen phosphate, and the ferroelectric sulfates, all contain hydrogen-oxygen bonds. The ferroelectric properties in these have been ascribed to the polarization of groups of atoms resulting from the displacement of a closely-associated hydrogen bond which thus furnished a "trigger" mechanism.

The second group is that of the water-insoluble, high-refractive index crystals containing oxygen octahedra, such crystals as barium titanate and potassium niobate. Here the ferroelectricity is ascribed to the high polarizability of the oxygen octahedra which leads to the "$4\pi/3$ catastrophe."

We have now found that the water-soluble double propionate, $Ca_2Sr(CH_3CH_2COO)_6$ is ferroelectric. It is improbable that this crystal[1] contains the H—O bond of the first group. Its low indexes of refraction ($\omega = 1.49$, $\epsilon = 1.50$) separates it from the crystals of the second group. It may, therefore, represent a third kind of ferroelectric crystal.

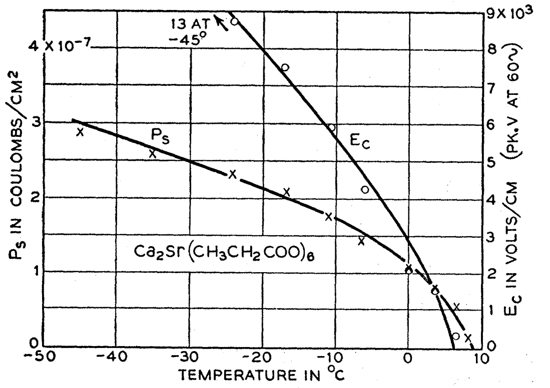

FIG. 1. Spontaneous polarization and the coercive field of $Ca_2Sr(CH_3CH_2COO)_6$.

The Curie temperature is 8.5°C. The ferroelectric axis is the tetragonal *c* axis. The behavior of the spontaneous polarization and the coercive field are given in Fig. 1.

There is one other isomorphous compound obtained through replacing the strontium by lead and we have not yet been able to detect any ferroelectricity.

It is undoubtedly more than premature to suggest any possible mechanism at the present moment. However, the hindered rotation of the CH_3 or even the C_2H_5 radical ought to be considered as the possible trigger. This would be analogous to the hindered NH_4^+ rotation in the ferroelectric phase of ammonium sulfate.

Our thanks are due to Dr. E. A. Wood, Mrs. V. B. Compton, and Dr. S. C. Abrahams for their constructive criticism.

[1] P. H. Groth, *Chemische Kristallographie* (W. Engelmann, Leipzig, 1910), Vol. 3, p. 203. Fitz and Sansoni, Z. Kryst. **6**, 68 (1882).

Sulfur Vacancy Emission in ZnS Phosphors

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RECENTLY, van Gool[1] has reported on an orange emission in CdS:Ag which has a maximum at 6200 A, and lies somewhat to the short-wavelength side of the normal Ag emission in CdS. This shorter wavelength emission was observed only when the amount of silver was present in excess of the amount of co-activator. van Gool suggested that the emission originates in the presence of either interstitial silver or sulfur vacancies, or of the two kinds of defects in association. From a study of the behavior of solid solutions of CdS and ZnS with Ag, van Gool stated the 6200 A peak in CdS:Ag would correspond to an emission in cubic ZnS:Ag at 3950 A.

Recently, we have observed such an emission band in cubic ZnS phosphors which contain no silver. Because the observed emission band has a peak at 3950 A, we believe it to be the same as that predicted by van Gool. This emission band was observed at 77°K and 3023 A excitation in specimens of ZnS:Cl, in ZnS containing 0.0001% copper without chloride, and in a specimen of pure ZnS fired for 36 hours at 1200°C and allowed to cool overnight.[2] We are therefore led to attribute the 3950 A band in ZnS to sulfur vacancies rather than to interstitial silver.

On the basis of van Gool's work, our result implies that a sulfur vacancy is responsible for the 6200 A emission in CdS and thus removes an uncertainty that has existed concerning this emission. Many workers have accepted a model of luminescence in sulfide phosphors proposed by Schön and Klasens[3] which describes the impurity states due to copper and silver