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.

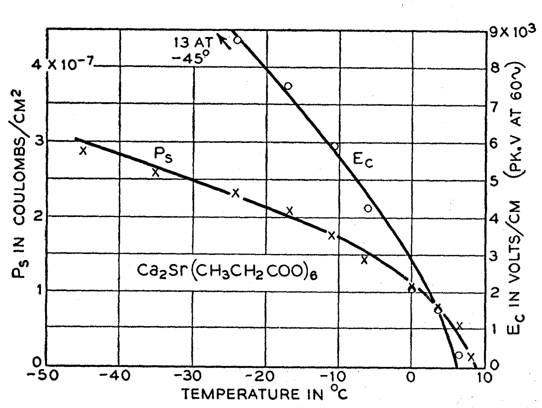

FIG. 1. Spontaneous polarization and the coercive field of $Ca_2Sr(CH_3CH_2COO)_6$.

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.

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[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 as ionized acceptor levels. The radiative transition, according to this model, is the capture of a conduction-band electron by a hole trapped at an acceptor level. Lambe and Klick,[4] however, have proposed an alternative model for the luminescence of CdS:Ag phosphors which describes the silver impurity states as vacant donor levels, and considers the radiative transition as the recombination of an electron trapped at such a donor level with a free hole. The experimental evidence they presented appears to support their model insofar as it supports the donor character of the luminescent centers.

We propose that the donor states studied by Lambe and Klick are associated with sulfur vacancies. Since the experiments of Lambe and Klick establish the donor nature of the centers without, however, establishing that the impurity levels are due to the silver introduced, their data permit this interpretation. Further, if sulfur vacancies are the origin of the donor centers responsible for the emission studies by Lambe and Klick, we can reconcile all of their experimental information with the Schön and Klasens model of Ag and Cu centers as acceptors. van Gool[1] has recognized this situation as a possibility.

It appears, therefore, that transitions of the kind described by Lambe and Klick are valid for donor levels such as those arising from sulfur vacancies, while the Schön-Klasens model may be used to describe the behavior of acceptors in ZnS and CdS.

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[1] W. van Gool, International Colloquium on Semiconductors and Phosphors, Garmisch, Germany, August 28–September 1, 1956 (unpublished); W. van Gool and H. A. Klasens, J. phys. radium **17**, 664 (1956).

[2] Prepared by Donald R. Hamilton, now at Westinghouse Research Laboratories.

[3] M. Schön, Z. Physik **119**, 463 (1942); H. A. Klasens, Nature **158**, 306 (1946); J. Electrochem. Soc. **100**, 72 (1953).

[4] J. Lambe and C. C. Klick, Phys. Rev. **98**, 909 (1955); J. Lambe, Phys. Rev. **98**, 985 (1955); **100**, 1586 (1955); Lambe, Klick, and Dexter, Phys. Rev. **103**, 1715 (1956); see also A. W. Smith, Phys. Rev. **101**, 1263 (1956).

Experimental Determination of the Noise Figure of an Ammonia Maser

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The recent theoretical work[1–3] on the noise produced by the active media of masers can be combined with previous microwave circuit theory[4] to yield a prediction for the noise figure of an ammonia maser.[5] We have measured the noise figure of an ammonia maser and compared the result with the predicted value.

A block diagram of the apparatus is shown in Fig. 1. Each maser was of the reflection type, i.e., there was only one microwave port in the maser cavity. The maser's output was separated from its input by a circulator.[6,7] The first maser was modulated on and off at 35 cps by applying a square-wave voltage between the two halves of the cavity.

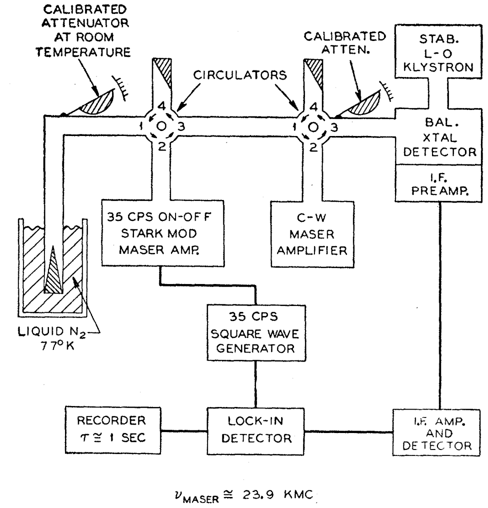

FIG. 1. Block diagram of apparatus.

The noise measurement consisted of changing the temperature of the input load by a known amount by changing the attenuation of the calibrated input attenuator and then varying the calibrated attenuator following the second maser in such an amount as to keep the dc recorder signal constant.

With the variable input attenuator at zero the loss between the liquid nitrogen cooled (77°) attenuator and the maser cavity was 0.69±0.10 db. These losses were at room temperature, 300°K. As a result, the thermal noise at the input to the maser cavity corresponded to a temperature of $77\times0.853+300\times0.147=110$°K. With the variable-input attenuator set at 20 db, the noise at the input to the maser cavity corresponded to a temperature of 298°K. When the effective input temperature of the maser was thus increased from 110°K to 298°K, the microwave power increase was measured to be 3.0±0.1 db. Thus the noise originating in the maser was equivalent to that which would result if the maser were noiseless but had, at its input, thermal radiation from a load at 78±20°K. In terms of noise figure,[8] F, this effective noise temperature is equivalent to $F=1+78/300=1.26$ or 1.0 db.[9]

The theoretical prediction of the effective noise temperature may be obtained by considering the maser as a lossless cavity with three suitably terminated ports. The cavity losses are represented by a port connected to a matched load at the cavity temperature, T_c. The actual microwave port is represented by a second port connected to the microwave line. The beam is represented by the third port terminated at an appropriate position by a susceptance $g(\nu)+jb(\nu)$ at the "effective beam temperature," T_B (negative for a maser). The frequency dependence of the susceptance