

TABLE I. Values of θ obtained from experimental determinations of r , and values obtained from x-ray studies.

	From r	From x-ray studies
Anthracene	33°	28.1° ^a
Phenanthrene	33.5°	35° ^b
Pyrene	38.5°	38.5° ^c
Chrysene	32.0° ^d	29.5° ^e

^a Sinclair, Robertson, and Mathieson, *Acta. Cryst.* **3**, 251 (1950).

^b B. S. Basak, *Indian J. Phys.* **24**, 309 (1950).

^c J. M. Robertson, *J. Chem. Soc.* **68A**, 358 (1947).

^d K. S. Krishnan and P. K. Seshan, *Indian Acad. Sci.* **8A**, 487 (1938).

^e J. Iball, *Proc. Roy. Soc. (London)* **A146**, 140 (1934).

state, prove that the π electrons—which are alone responsible for the phenomena mentioned above—migrate in the plane of the molecule. Recent publications¹⁰ on conjugated hydrocarbons based on LCAO molecular orbital theory yield results regarding energy levels, free valence, and reactivities, etc., which are in agreement with experimental results. Our published results^{1,2} derived with the assumption of a linear oscillator are in agreement with values derived from present considerations. From all these, it appears to be reasonable to assume the oscillators of these molecules of anthracene, phenanthrene, pyrene, chrysene, etc., to be equivalent to linear oscillators. Since the

¹⁰ C. W. Scherr, *J. Chem. Phys.* **9**, 1582 (1953); K. Raedenberg and C. W. Scherr, *J. Chem. Phys.* **9**, 1565 (1953).

molecular planes of these crystals are not exactly at 90°, we find, quite reasonably, a little difference between the θ obtained from the x-ray result and the θ obtained from r , the ratio of intensities of fluorescence along b and along a . If the angle of the molecular plane with the b axis in the c face is other than 90°, it is not at all difficult to calculate the ratio of intensity along b and a .

In crystals where the plane of the molecule is normal to the c face on which light is incident normally, r (I_b/I_a) remains the same, whatever may be the direction of incident light vector. So, conversely, from the constant value of ratio of intensities along b and a , one can easily find the angle subtended by the plane of the molecule in the c face. It should be stated here that other conditions may also give similar results but they can be very easily eliminated, and so without any x-ray results, from a careful study of intensity of fluorescence along different perpendicular directions it is possible to find out the orientation of the molecules in a crystal and the nature of the oscillators responsible for such emission.

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Dielectric Constant Behavior of Single-Domain, Single Crystals of Barium Titanate in the Vicinity of the Curie Point

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The dielectric constant of single crystals of barium titanate has been measured in the vicinity of the Curie point. An abrupt transition is observed substantiating earlier conclusions that the transition is first order. The Curie constant¹ was found to be 1.73×10^6 °C. The data indicate a thermal hysteresis effect.

CROSS¹ has indicated that the dielectric constant of barium titanate should increase discontinuously at the Curie point whereas published experimental data does not bear this out.^{1,2}

We have made similar measurements using our equipment which automatically plots the dielectric constant as a function of temperature on a Leeds and Northrup X-Y recorder. The results are shown in Fig. 1. It can be seen that the dielectric constant does indeed rise abruptly at the Curie point. This is additional evidence indicating that the Curie transition in barium titanate is first order.

Of interest also is the temperature hysteresis effect not indicated by the measurements of Cross and Merz but observed optically by Forsbergh,³ thermally by Roberts,⁴ and electrically by Kanzig and Maikoff.⁵ Such an effect is expected on the basis of Devonshire's theory, however, the width is only 2°C to be compared with the 7°C expected in the absence of thermal fluctuations. Forsbergh's³ measurements indicated a temperature difference of only 0.7°C for zero applied pressure. However, the transition in his case occurred at about 107.5°C. When the pressure was raised until the transi-

¹ L. E. Cross, *Phil. Mag.* **44**, 1161 (1953).

² W. J. Merz, *Phys. Rev.* **91**, 513 (1953).

³ P. W. Forsbergh, *Phys. Rev.* **93**, 686 (1954).

⁴ S. Roberts, *Phys. Rev.* **85**, 925 (1952).

⁵ W. Kanzig and N. Maikoff, *Helv. Phys. Acta.* **24**, 343 (1951).

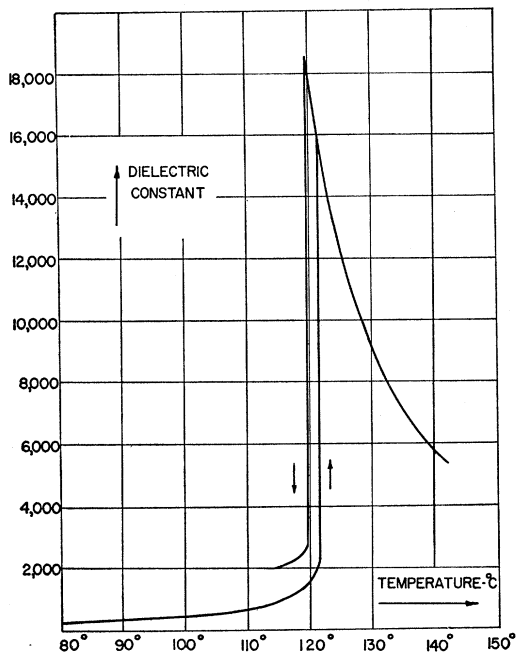


FIG. 1. Dielectric constant as a function of temperature.

tion temperature became equal to ours (about 120°C), the temperature difference became equal to that observed by us. It is believed that the lower temperature difference was due to addition agents not present in our crystals.

The Curie-Weiss plot is shown in Fig. 2, and it is seen that the Curie-Weiss law is followed completely. The Curie constant is 1.73×10^5 °C. This is to be compared with 1.56×10^5 as observed by Merz.²

After going through the temperature cycle it is

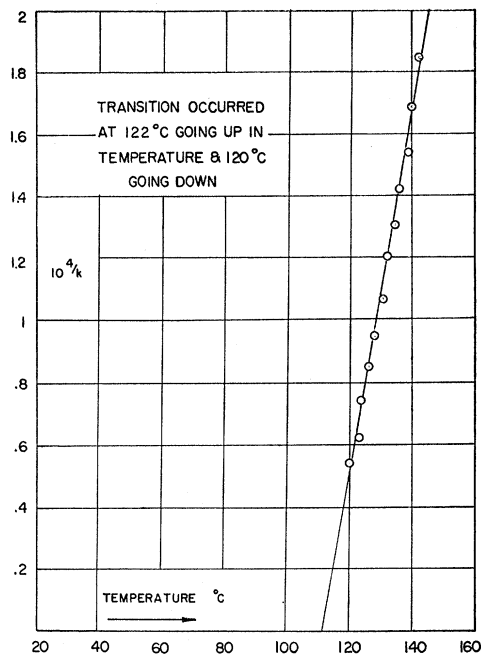


FIG. 2. Reciprocal dielectric constant vs temperature.

noted that the dielectric constant is higher than before. This is due to the fact that the polarization is no longer uniformly perpendicular to the surface of the crystal. Consequently, there are contributions from the high dielectric constant in the "a" direction from regions where the polarization is parallel to the surface.

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