

Temperature Variation of Magnetic Anisotropy of Organic Crystals

As has been shown by Krishnan¹ and his collaborators, the study of the magnetic anisotropy of organic crystals enables us in many cases to determine the orientation of the molecules in the crystal lattice. A natural extension of this important line of work, suggested to me by Sir C. V. Raman, is the investigation of the effect of temperature on magnetic anisotropy, which may be expected to yield valuable information regarding the character of the thermal motions (for example, oscillations and hindered or free rotations) of the molecules in the crystal lattice and to elucidate the mechanism of fusion.

I have carried out measurements in the case of resorcinol over a range of temperature from 26° C. up to the melting point (110° C.) of the substance. Resorcinol was chosen because the crystal is stable and does not volatilize easily. The structure of the crystal has been studied by Robertson² by X-ray analysis, and the magnetic anisotropy at room temperature has also been determined by K. Lonsdale³. The method described by Krishnan⁴ was adopted for the measurement of anisotropy, a modified technique being employed for fixing the crystal at the end of the quartz fibre and for making the measurements at the higher temperatures.

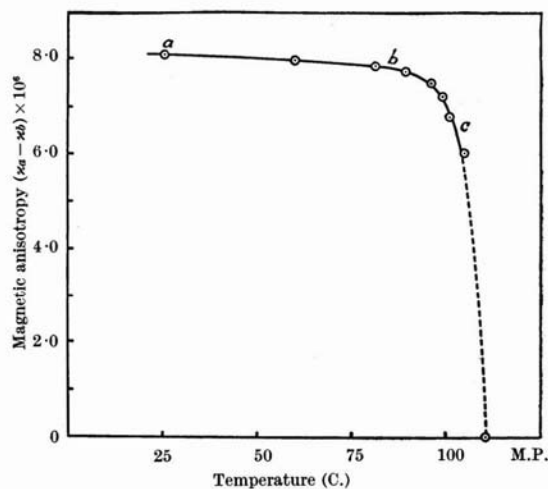


Fig. 1.

The following experimental procedure was adopted. For any setting of the crystal, the magnetic anisotropy in the plane concerned was first of all determined at room temperature. The crystal was then raised to the desired temperature by electrically heating the surrounding tube, the temperature at the region near the crystal being measured by means of a calibrated thermo-element. The magnetic anisotropy at the high temperature was then measured. The crystal was finally allowed to cool down to room temperature and the anisotropy again measured. It was found that when the high temperature did not exceed 105° C., the initial value of the anisotropy was almost fully restored. In all cases the mean of the initial and the final values of the magnetic anisotropy at room temperature was used in the calculations.

The variation of the magnetic anisotropy with temperature when the crystal is suspended with the *c* axis vertical is shown in Fig. 1. Up to about 15° C. below the melting point, the change of anisotropy is comparatively small. From *b* to *c* on the curve the variation is pronounced. From *c* onwards the transition is very rapid, indicating a state of instability. When the crystal was heated until it began to melt, the anisotropy practically disappeared. It is significant that the effect of temperature becomes prominent only in the vicinity of the melting point.

A determination of the magnetic anisotropy of resorcinol at room temperature gave the values: $\chi_a - \chi_b = 8.13 \times 10^{-6}$, $\chi_c - \chi_b = 13.30 \times 10^{-6}$, $\chi_c - \chi_a = 5.22 \times 10^{-6}$, whence assuming Pascal's value -67.2×10^{-6} , for the mean susceptibility, we get $\chi_a = -66.2 \times 10^{-6}$, $\chi_b = -74.3 \times 10^{-6}$, $\chi_c = -61.0 \times 10^{-6}$, and $\alpha = 55.9^\circ$, $\beta = 47.0^\circ$, $\gamma = 62.1^\circ$, in satisfactory agreement with the results of K. Lonsdale.

I have also made a preliminary investigation of the magnetic anisotropy of ammonium nitrate at different temperatures up to the melting point of the crystal. The magneocrystallic data seem to lend support to the findings of X-ray analysis⁵ in regard to the variation of the crystalline structure of ammonium nitrate with temperature.

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¹ Krishnan, K. S., Guha, B. C., and Banerjee, S., *Phil. Trans.*, A, **231**, 235 (1933).

² Robertson, J. M., *Proc. Roy. Soc.*, A, **157**, 79 (1936).

³ Lonsdale, K., *NATURE*, **137**, 826 (1936).

⁴ Krishnan, K. S., and Banerjee, S., *Phil. Trans.*, A, **234**, 265 (1935).

⁵ Hendricks, S. B., Posnjak, J., and Kracke, E. C., *J. Amer. Chem. Soc.*, **54**, 2766 (1932).