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- ¹ See, for example, Snoek, J. L., "New Developments in Ferromagnetic Materials" (Elsevier, 1947).
² Went, J. J., Rathenau, G. W., Gorter, E. W., and van Oosterhout, G. W., *Philips Tech. Rev.*, **14**, 33 (1952).
³ Smiltens, J., and Fryklund, D. H., Progress Report V, Mass Inst. Tech., p. 58 (1949).
⁴ Galt, J. K., Matthias, B. T., and Remeika, J. P., *Phys. Rev.*, **79**, 39 (1950).
⁵ Galt, J. K., Yager, W. A., Remeika, J. P., and Merritt, F. R., *Phys. Rev.*, **81**, 470 (1951).
⁶ de Boer, J. H., and Verwey, E. J. W., *Proc. Phys. Soc., A*, **59**, 59 (1937).
⁷ Darken, L. S., and Gurry, R. W., *J. Amer. Chem. Soc.*, **68**, 798 (1946).
⁸ Gurry, R. W., and Darken, L. S., *J. Amer. Chem. Soc.*, **72**, 3906 (1950).
⁹ Adelsköld, V., *Ark. Kemi, Mineral. Geol.*, **12A**, 1 (1938).
¹⁰ Braun, P. B., see following communication.

Crystal Structure of BaFe₁₈O₂₇

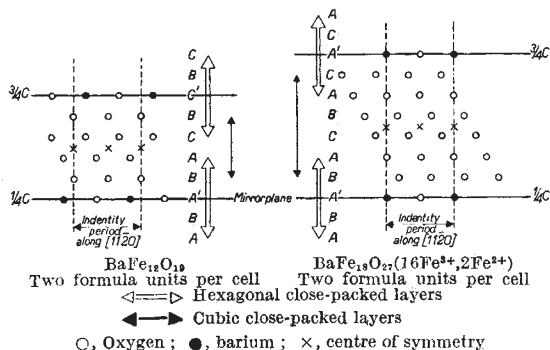
IN the course of an investigation¹ into the properties of substances with magnetoplumbite structure², Wijn³ of these laboratories tried to prepare single crystals of BaO.6Fe₂O₃. Mixtures of barium oxide and magnetite (Fe₃O₄) were melted and slowly cooled. In one of these melts a single crystal of about 4 × 5 × 0.3 mm.³ developed.

The results of the X-ray investigation of this crystal are shown below. The notation used is that of the "International Tables for the Determination of Crystal Structures" (1935).

Composition, BaFe ₁₈ O ₂₇		Space group C6/mmc	
<i>a</i> = 5.88 Å. <i>c</i> = 32.84 Å.		2 formula units per cell	
2 Ba	2(b)	6 O	in 6(h) <i>x</i> ~ 180°
2 Fe	2(d)	12 O	" 12(k) <i>z</i> = 64.5° <i>x</i> ~ 60°
4 Fe	4(f) <i>z</i> = 75°	4 O	" 4(f) <i>z</i> = 64.5°
4 Fe	4(e) <i>z</i> = 20°	12 O	" 12(k) <i>z</i> = 40° <i>x</i> ~ 180°
4 Fe	4(f) <i>z</i> = 26.8°	4 O	" 4(e) <i>z</i> = 40°
4 Fe	4(f) <i>z</i> = 33.5°	12 O	" 12(h) <i>z</i> = 13° <i>x</i> ~ 60°
6 Fe	6(g)	4 O	" 4(f) <i>z</i> = 13°
12 Fe	12(k) <i>z</i> ~ 54° <i>x</i> ~ 60°		

The magnetoplumbite structure can be described as consisting of spinel-like blocks, with the thickness of four oxygen layers, linked together by layers in which one oxygen has been replaced by barium. The linking layer is hexagonally packed with respect to its neighbouring layers. Moreover, it contains an iron atom surrounded by five oxygen atoms in a trigonal dipyrmaid.

The new structure described here is built along the same lines. The spinel block has not four but six oxygen layers, the Ba/Fe ratio now being 1/18.



A detailed discussion of the structure determination will be published elsewhere.

The accompanying drawings show the relation between the two structures mentioned. They represent sections through the 0001 and 1120 axes. All iron atoms are omitted; they are distributed regularly among the cavities in the close packing of oxygen and barium.

P. B. BRAUN

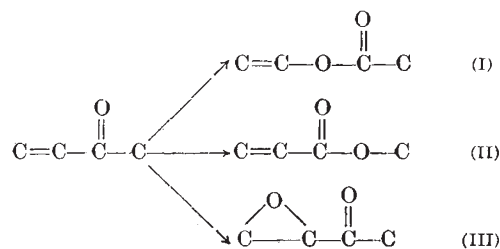
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- ¹ Went, J. J., Rathenau, G. W., Gorter, E. W., and van Oosterhout, G. W., *Philips Tech. Rev.*, **B**, 194 (1951-52); *Phys. Rev.*, **86**, No. 3, 424 (1952).
² Adelsköld, V., *Ark. Kemi, Mineral. Geol.*, **12A**, No. 29 (1938).
³ Wijn, H. P. J., see preceding communication.

Peroxidation of Unsaturated Ketones

Two recent reviews of peroxidation of organic compounds^{1,2} cite the fact that α,β -unsaturated ketones are oxidized by peracids to enol esters. *A priori*, however, one might expect one or more of three possible products and their hydrolysates.



Thus, I and II would result from an attack of peracid at the carbonyl carbon followed by rearrangement according to the mechanism proposed by Criegee³, Friess⁴, and Doering⁵, while III would be the consequence of an attack at the β -carbon of the conjugated system.

With the exception of a few peroxidation reactions in the terpene field, only three main examples⁶⁻⁸ of this process appear in the literature, and in all three cases the starting compounds possess a phenyl group in the β -position. On applying the accepted mechanism³⁻⁵ to this system (for example, benzalacetone), it becomes apparent that the transition state involves a mesomeric benzyl carbonium ion (IV) if the electron-rich carbon-carbon double bond is permitted to participate in breaking the peroxide linkage. Since (IV) constitutes a low-energy state, it would be expected that the above transition requires less activation energy than either the migration of the methyl group (to yield II) or an original attack of the peracid molecule on the β -carbon (to yield III). Thus, it might be predicted that any α,β -unsaturated carbonyl system containing a substituent in the β -position, which has the power of stabilizing a carbonium ion there, would yield an enol ester or lactone on peracid oxidation. Furthermore, systems not having this property might be expected to yield the same, and/or α,β -unsaturated esters or lactones and/or α,β -epoxy-ketones.

Julian's perbenzoic acid oxidation⁹ of 5,6-dibromo-16-pregnen-3 β -ol-20-one acetate (V) to the 16,17-oxido compound (VI) lends some credence to the above argument. Likewise, preliminary experi-