Fig. 2.—Absorption spectrum of Cs_2CoCl_4 dispersed in KBr ("thin" preparation) at liquid nitrogen temperatures, against arbitrary diaphragm air blank; condensed and spread wave length scale tracings, to show general features and resolution of peaks.
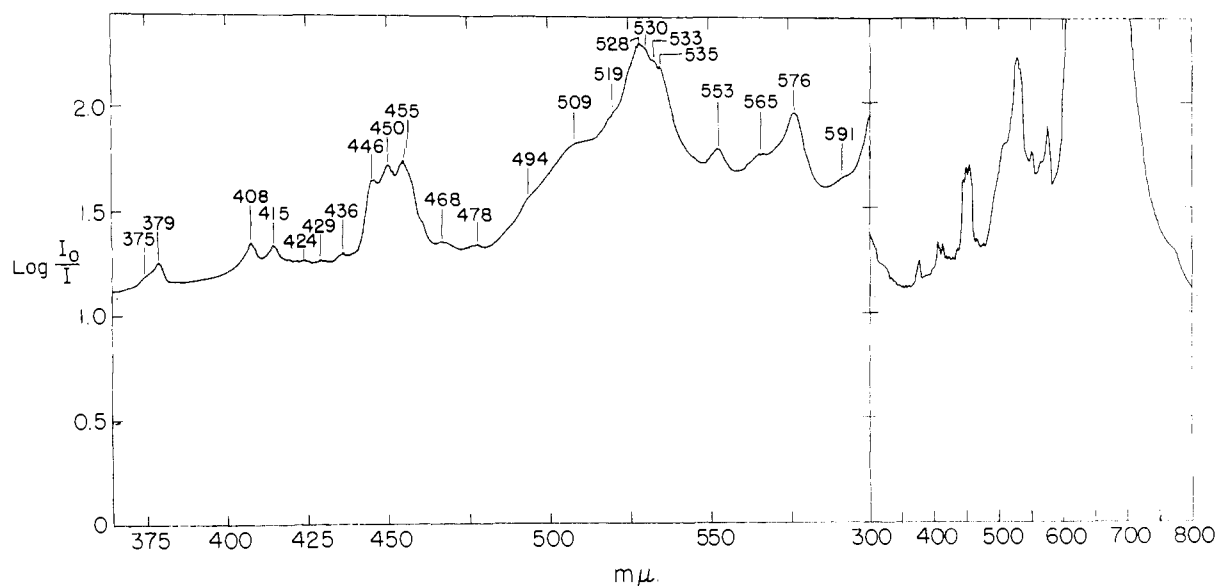

Fig. 3.—Absorption spectrum of Cs_2CoCl_4 dispersed in KBr ("thick" preparation) at liquid nitrogen temperatures, against equivalent KBr blank; condensed and spread wave length scale tracings, to show general features and resolution of peaks.

is exaggerated at low temperatures, even at room temperature the absorption at about 700 mμ dominates the shoulder at 675 mμ, and is about twice the absorption at 650 mμ. The room temperature spectrum resembles to a large extent the published curves for cobalt in HI solution.[8,9] In the solution (Fig. 1), the absorptions at 691 and 661 mμ are fairly well resolved, though there may be a hint of a peak at about 680 mμ[8–10] which does not show well in the tracing.

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Barium Iron Oxide Isomorphs of Hexagonal and Tetragonal BaTiO$_3$

BY W. W. MALINOFSKY AND H. KEDESDY

Investigations of the formation of magnetic barium iron oxide led to the study of the reaction product obtained from a $2BaCO_3$–Fe_2O_3 powder mixture fired at 900° in oxygen. The composition of the barium iron oxide reaction product from this mixture should be close to $BaFeO_3$, analogous to BaTiO$_3$. A reaction product of that approximate composition was reported in an earlier investigation of
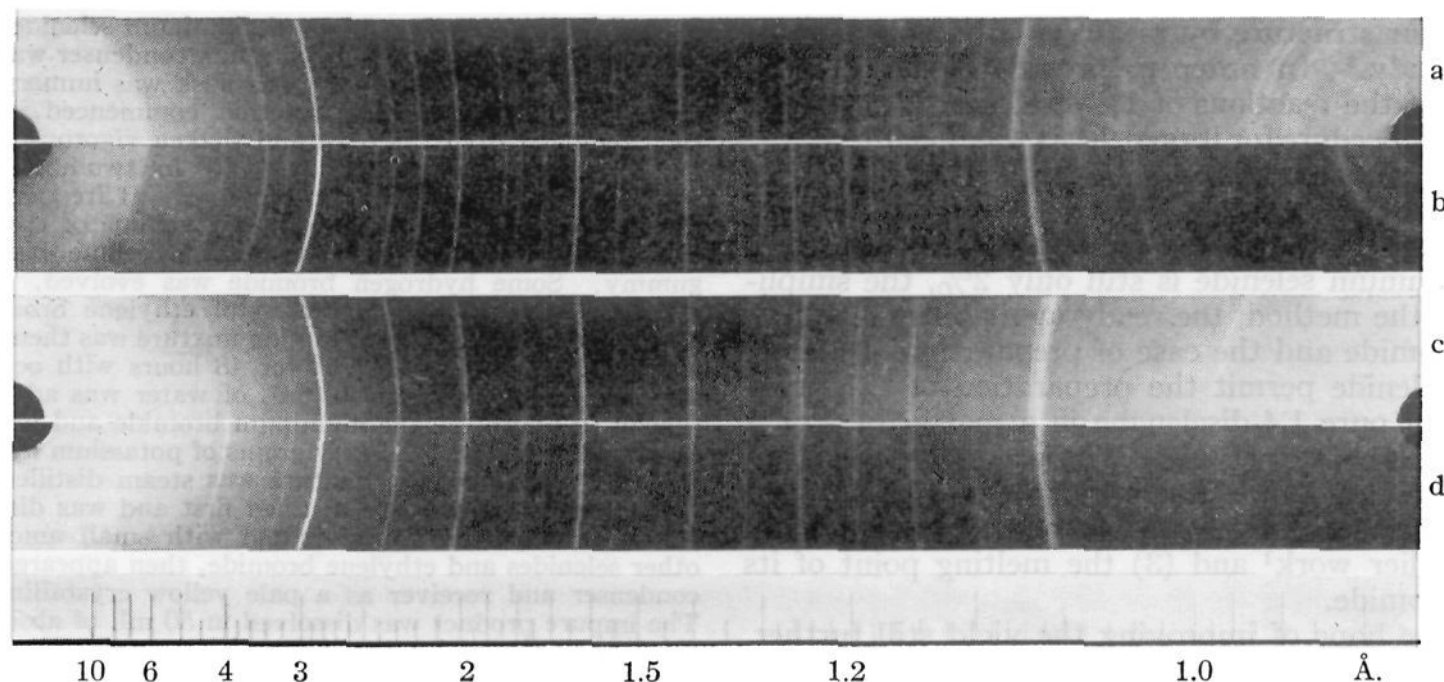
Fig. 1.—Comparison of X-ray diffraction patterns of Ba–Fe–oxide and BaTiO₃ polymorphs; camera radius 57.3 mm., filtered Fe radiation: a, BaTiO₃, hex.; b, Ba–Fe–oxide, hex.; c, BaTiO₃, tetr.; d, Ba–Fe–oxide, tetr.

the $BaCO_3$–Fe_2O_3 system by Erchak, Fankuchen and Ward.[1] The X-ray diffraction pattern of their product, and the approximately ABO_3 composition, suggested to those authors a perovskite-type structure. The presence of certain extra lines in the pattern, however, led them to adopt instead a larger cubic cell composed of eight perovskite basic units. This larger face-centered cell ($a_0 = 8.05$ Å.) was interpreted as due to an ordered distribution of oxygen vacancies corresponding to the chemically-indicated composition $Ba_8Fe_8O_{21}$. The diffraction pattern of the reaction product recently obtained by us was found to be essentially the same as that reported by the authors mentioned above. Studied in the light of information now available concerning the polymorphic structures exhibited by $BaTiO_3$, however, the pattern of this product can be indexed in the hexagonal system, and in fact, it matches very well the pattern of the hexagonal polymorph of $BaTiO_3$ (Fig. 1).

Encouraged by these results, we investigated the possibility of the occurrence of the other analogous polymorphs with cubic or pseudo-cubic structures. Firing the hexagonal barium iron oxide at 1275° in oxygen and slow-cooling resulted in the tetragonal polymorph. Here also, a comparison with the corresponding X-ray diffraction pattern of tetragonal $BaTiO_3$ showed good agreement. A few weak extra lines, however, indicate the presence of some hexagonal phase material, probably due to the slow-cooling. The evaluation of the hexagonal and tetragonal forms of the barium iron oxide and the comparison with $BaTiO_3$ are shown in Table I. The unit cell dimensions determined

show that in both cases the barium iron oxide analogs are slightly smaller than those of $BaTiO_3$. This indicates that the iron ion is slightly smaller than the corresponding titanium ion.

The ideal chemical formula $BaFeO_3$, barium metaferrate(IV), implies an iron oxidation state of four, which is rare. The more common iron valence, three, would lead to compositions lying in the range between $BaFeO_{2.5}$ and $Ba_{1.2}Fe_{1.2}O_3$, but neither a 16% deficiency of oxygen, nor a 20% surplus of barium is likely in a stable perovskite structure. A more plausible alternative is the co-presence of Fe(III) and Fe(IV) in the same structure with a corresponding increase in the number of oxygens per molecule toward three. This alternative is favored by the results of preliminary measurements of electrical conductivity on pellets of the reaction product. It is worthwhile to note that of the two polymorphic modifications of barium iron oxide, the hexagonal form seems to be more stable at low temperatures, the tetragonal at higher, which is just the reverse of the situation in the $BaTiO_3$. In a future paper the stability, formation conditions and electrical and magnetic properties of these barium iron oxide polymorphs will be described in greater detail.

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TABLE I

Unit cell	Barium iron oxide	BaTiO₃	Structure
a_0, Å.	5.68	5.74	
c_0	13.86	14.05	Hexagonal
c_0/a_0	2.44	2.45	
a_0, Å.	3.98	3.99	
c_0	4.01	4.03	Tetragonal
c_0/a_0	1.01	1.01	

(1) M. Erchak, Jr., I. Fankuchen and R. Ward, THIS JOURNAL, 68, 2085 (1946).

A New Synthesis of 1,4-Diselenane. The 1,1,4,4-Diselenane Tetrahalides

BY J. D. MCCULLOUGH AND N. W. TIDESWELL

The cyclic selenide 1,4-diselenane was first prepared by the reaction of lithium selenide on β,β'-dichlorodiethyl selenide in anhydrous acetone.[1] Although the yield was only 0.3%, the substance was unambiguously identified through selenium analysis and a complete determination of its crystal and

(1) E. S. Gould and J. D. McCullough, THIS JOURNAL, 73, 1105 (1951).