

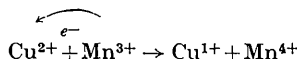
Table 2

Cations	r (Å)	Outer electronic configuration	Most probable* bond formation
Cd ²⁺	0.97	4d ¹⁰	sp^3
Mn ²⁺	0.91	3d ⁵	sp^3
Mn ³⁺	0.62	3d ⁴	dsp^2
Mg ²⁺	0.78	2p ⁶	Electrovalent
Zn ²⁺	0.78	3d ¹⁰	sp^3
Co ²⁺	0.82	3d ⁷	sp^3 ; dsp^2
Fe ²⁺	0.82	3d ⁶	sp^3 ; d^2sp^3
Fe ³⁺	0.60	3d ⁵	sp^3
Cu ¹⁺	0.96	3d ¹⁰	sp^3
Cu ²⁺	0.70	3d ⁹	dsp^2
Ni ²⁺	0.78	3d ⁸	dsp^2

* Goodenough & Loeb (1955).

sites, some Mn³⁺ ions being displaced from octahedral sites.

The occurrence of cubic symmetry with a normal cation arrangement of copper manganite is contrary to expectation since, of all the metals in the first transition series, Cu²⁺ has the strongest square (dsp^2) bond-forming power and should occupy an octahedral site, thus making the structure inverse and the symmetry tetragonal. The result can easily be explained on the basis of an electron transfer process

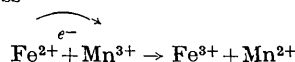


occurring under the experimental conditions and, as a result, the Cu¹⁺ ions formed occupy tetrahedral sites (Table 2), the resulting structure being normal. Furthermore, in the unit cell of Cu¹⁺[Mn³⁺Mn⁴⁺]O₄²⁻, the 8 Mn⁴⁺ ions (3d⁰) form six equivalent octahedral d^2sp^3 bonds and the 8 Mn³⁺ ions dsp^2 square bonds. The stress produced by the Mn³⁺ ions, which occupy only 25% of the octahedral lattice sites, is not sufficient to cause any observable distortion in the macro-crystal.

The inverse structure of nickel manganite shows the stronger tendency for Ni²⁺ ions to occupy octahedral sites. However, if the Ni²⁺ ions also form dsp^2 bonds, all the octahedral ions tend to distort the lattice, and the observed cubic symmetry is thus anomalous. This may,

however, be explained in one of the following ways: (i) Ni²⁺ ions form six equivalent bonds of the type $3d^24s4p^3$ by promoting two 3d electrons to higher 5s level or $4s4p^34d^2$ hybridized orbitals in the octahedral site; (ii) the group of four planar dsp^2 bonds due to Mn³⁺ and Ni²⁺ ions forming tetragonally distorted octahedra oriented in three mutually perpendicular directions; or (iii) a compound Mn²⁺[Ni²⁺Mn⁴⁺]O₄²⁻ formed as a result of the electron transfer process, $2 \text{Mn}^{3+} \rightarrow \text{Mn}_2^{2+} + \text{Mn}^{4+}$. The cubic symmetry can then be explained as in the case of Cu¹⁺[Mn³⁺Mn⁴⁺]O₄²⁻.

In the case of iron manganite, it is not possible to determine the cation arrangement from the X-ray data because of the nearly equal scattering power of the two cations. However, since c/a is almost equal to unity, it can be inferred that at octahedral sites an appreciable portion of Mn³⁺ ions have been replaced by cations forming six equivalent bonds. It is likely that an electron transfer process



occurs so that a compound Fe_{0.5}³⁺Mn_{0.5}²⁺[Fe_{0.5}²⁺Mn_{1.5}³⁺]O₄²⁻ with an almost random type of structure is formed.

Further work is under progress and the detailed results will be published later.

We are grateful to Prof. G. I. Finch for his valuable advice and continued interest in this work. We also thank Mr J. S. Gujral for his help in the experimental work.

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Acta Cryst. (1957). **10**, 440

Observations on pigeonite. By M. G. BOWN and P. GAY, *Department of Mineralogy and Petrology, Cambridge, England*

(Received 4 March 1957)

The most important rock-forming pyroxenes occur in the ternary system MgSiO₃-FeSiO₃-CaSiO₃, with less than 50% CaSiO₃; a minor amount of replacement by other cations, notably aluminium, is usual. Over most of this field the pyroxenes are monoclinic, although at less than 5% CaSiO₃ an orthorhombic modification is the more stable form. All clino-pyroxenes are very similar in structure to diopside, CaMg(SiO₃)₂, which has the space group *C2/c* (Warren & Bragg, 1929; Warren & Bischof, 1931). Those with compositions falling inside the trapezium CaMgSi₂O₆-CaFeSi₂O₆-FeSiO₃-MgSiO₃ are divided, on the basis of their optical properties, into augites and pigeonites: roughly speaking augites contain more than,

and pigeonites less than, 20% CaSiO₃. There is a solid-solubility gap at low temperatures between augite and pigeonite, the variation of the solubilities of one component in the other being temperature dependent; thus augite which has crystallized at a fairly high temperature may precipitate lamellae of pigeonite on slow cooling in the earth's crust, and similarly pigeonite crystals often contain augite lamellae. Morimoto (1956) has recently examined such a lamellar aggregate, and has found that the cell dimensions of the pigeonite are very similar to those of the augite, that the two phases have the directions of the x and y axes in common, and that whereas the space group of the augite is *C2/c*, that of the pigeonite

is $P2_1/c$. For future reference we will term the reflexions with $h+k$ even, given by both phases, class (a) reflexions, and those with $h+k$ odd, given only by the pigeonite, class (b) reflexions.

Before learning of Morimoto's work we had examined pigeonites from several localities, and had also established the primitive lattice, and the orientation of the two phases in lamellar intergrowths: we have subsequently confirmed the space group. Further, for some of the specimens the class (b) reflexions from pigeonite were observed to be slightly, but definitely, diffuse compared with those of class (a). The reason for this is not yet known; there is no obvious correlation of the diffuseness either with the composition or with the probable thermal state separately. For a given rock both the pigeonite in the 'augite' crystals and that in the 'pigeonite' crystals are consistent in respect of this diffuseness. One volcanic pyroxene, a pigeonite described by Hallimond (1914) occurring as small rounded crystals in an andesitic pitchstone from Mull, has been examined. This rock has been cooled so quickly that no augite has precipitated from the pigeonite. The space group is again $P2_1/c$, and the class (b) spots are slightly diffuse, but no more so than for several of the slowly cooled pigeonites. It seems, therefore, that the primitive lattice is not a property of a low-temperature form of pigeonite only. Preliminary heating

experiments have confirmed this; a single crystal showed no obvious change in intensity of the class (b) reflexions after being heated at 1000° C. for 2 days, followed by rapid cooling in air.

It was further noticed that the class (a) spots from the pigeonite and augite were joined by a streak on the photographs for some lamellar specimens, but not for others. This streak is presumably caused by a gradual change in cell dimensions at the junction of the lamellae and the host crystal. There is no correlation between the intensity of the streak and the diffuseness of the class (b) reflexions. For the limited number of specimens examined it appears that the streak is strong if the lamellae are relatively coarse, and absent if they are very fine.

Further work is in progress. We would like to thank Dr N. Morimoto for making his results available to us before publication.

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Notes and News

Announcements and other items of crystallographic interest will be published under this heading at the discretion of the Editorial Board. Copy should be sent direct to the British Co-editor (R. C. Evans, Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England).

Acta Crystallographica

For the convenience of subscribers who prefer to bind the annual volume in two sections a title page for the period January–June 1957 is enclosed with this issue. A corresponding title page for the period July–December 1957 and also a title page for the whole year will be distributed with the December issue.

Crystallographic studies of perovskite-like compounds. IV: correction

In the above article by S. Geller (*Acta Cryst.* (1957), **10**, 243) the author requests that on p. 247 the three sentences 'Yakel has also examined . . . compound by solid–solid reaction' be deleted.

Conference on Scientific Information

An international conference on Scientific Information will be held in Washington, D.C., U.S.A., in November 1958. This Conference is being sponsored by the National Academy of Sciences–National Research Council of the U.S.A., the National Science Foundation and the American Documentation Institute. The areas covered by the agenda of the conference are the following:

- (1) Requirements of scientists for scientific literature

and reference services: knowledge now available and methods of ascertaining their requirements.

- (2) The function and effectiveness of abstracting and indexing services for storage and retrieval of scientific information.
- (3) Effectiveness of scientific monographs, compendia, and specialized information centres in meeting the needs of scientists: present trends and new and proposed techniques and types of services.
- (4) Organization of information for storage and search: comparative characteristics of existing systems.
- (5) Organization of knowledge for storage and retrospective search: intellectual problems and equipment considerations in the design of new systems.
- (6) Organization of information for storage and retrospective search: possibility for a general theory of storage and search.
- (7) Responsibilities of governmental bodies, professional societies, universities, and research and industrial organizations to provide improved information services and to promote research in documentation.

Persons who wish further information concerning the conference are requested to write to the Executive Secretary, Dr Alberto F. Thompson, National Academy of Sciences, 2101 Constitution Avenue, Washington 25, D.C., U.S.A.