

Progress in Solid-State Chemistry Vol. 5

Editor: HOWARD REISS

Department of Chemistry, University of California, Los Angeles



Progress in Solid-State Chemistry Series

PERGAMON

8061360
5

R378
V.5

PROGRESS IN SOLID STATE CHEMISTRY

VOLUME 5



H. REISS

Department of Chemistry
University of California
Los Angeles



E8051360



PERGAMON PRESS

Oxford · New York · Toronto

Sydney · Braunschweig

Pergamon Press Ltd., Headington Hill Hall, Oxford
Pergamon Press Inc., Maxwell House, Fairview Park, Elmsford, New York 10523
Pergamon of Canada Ltd., 207 Queen's Quay West, Toronto 1
Pergamon Press (Aust.) Pty. Ltd., 19a Boundary Street, Rushcutters Bay,
N.S.W. 2011, Australia
Vieweg & Sohn GmbH, Burgplatz 1, Braunschweig

Copyright © 1971 Pergamon Press Ltd.

All Rights Reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior permission of Pergamon Press Ltd.

First Edition 1971

Library of Congress Catalog Card No. 63-11362

Printed in Great Britain by A. Wheaton & Co., Exeter

08 015846 3

PROGRESS IN SOLID STATE
CHEMISTRY

VOLUME 5

EDITORIAL ADVISORY COMMITTEE

DR. ROBERT S. BARNES (BISRA/The Inter-Group Laboratories, 24 Buckingham Gate, London, S.W.1, England)

PROFESSOR LEO BREWER (Inorganic Materials Research Division, Latimer Hall, Lawrence Radiation Laboratory, Berkeley, California 94720)

DR. SEYMOUR GELLER (North American Rockwell Science Center, P.O. Box 1085, Thousand Oaks, California 91360)

DR. N. B. HANNAY (Research Materials Division, Bell Telephone Laboratories, Murray Hill, New Jersey 07974)

PROFESSOR F. A. KRÖGER (Electrical Engineering Department, University of Southern California, University Park, Los Angeles, California 90007)

PROFESSOR A. W. LAWSON (Department of Physics, University of California, Riverside, California 92502)

DR. G. G. LIBOWITZ (Ledgemont Laboratory, Kennecott Copper Corporation, 128 Spring Street, Lexington, Massachusetts 02173)

PROFESSOR PER-OLOV LÖWDIN (Quantum Chemistry Group, University of Uppsala, Uppsala, Sweden)

DR. J. J. LANDER (Chemical Electronics Research Department, Bell Telephone Laboratories, Murray Hill, New Jersey 07974)

DR. ARNOLD MILLER (Whittaker Corporation, 6055 East Washington Blvd., Suite 1029, Los Angeles, California 90022)

PROFESSOR ERICH MOLLWO (Friedrich-Alexander-Universität zu Erlangen-Nürnberg, Schlossplatz 4, Erlangen, Germany)

PROFESSOR R. SMOLUCHOWSKI (Solid State and Materials Programme, Duffield Hall, Princeton University, Princeton, New Jersey 08540)

DR. J. P. SUCHET (Centre National de la Recherche Scientifique, Paris, France)

PROFESSOR F. C. TOMPKINS (Department of Chemistry, Imperial College of Science and Technology, Imperial Institute Road, London, S.W.7, England)

PREFACE

VOLUME 5 is devoted primarily to the *structural chemistry* of solids and to the influence of such structure on chemical and physical properties.

LIST OF CONTRIBUTORS

CRYSTAL CHEMISTRY AND MAGNETIC STRUCTURES OF SUBSTITUTED $\text{Ca}_2\text{Fe}\text{O}_5$

S. GELLER, R. W. GRANT and U. GONSER

North American Rockwell Science Center, P.O. Box 1085, Thousand Oaks, California 91360

STRUKTURCHEMIE EINIGER VERBINDUNGEN DER ÜBERGANGSMETALLE MIT DEN ELEMENTEN C, Si, Ge, Sn

VON HANS NOWOTNY

Institut für physikalische Chemie, Universität Wien, Austria

LES BRONZES OXYGENES

PAUL HAGENMULLER

Faculté des Sciences, Université de Bordeaux, 351 cours de la Liberation, 33—Talence, France

METALLIC OXIDES

JOHN B. GOODENOUGH

Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts 02173

ELECTRONIC STRUCTURE, COLORATION AND PHOTODECOMPOSITION OF THE ALKALI-METAL AZIDES

D. A. YOUNG

Imperial College, London, S.W.7, England

DIPOLAR IMPURITIES IN ALKALI HALIDES: ZEEMAN AND STARK EFFECTS OF $\text{Sm}^{2+}:\text{K}^+$ VACANCY PAIR FLUORESCENCE, AND PARAELECTRIC RESONANCE AND RELAXATION OF OH^- in KCl

L. A. VREDEVOE

North American Rockwell Science Center, P.O. Box 1085, Thousand Oaks, California 91360

and

C. R. CHILVER and F. K. FONG

Department of Chemistry, Purdue University, Lafayette, Indiana 47907



CONTENTS

| | |
|--|-----|
| PREFACE | ix |
| LIST OF CONTRIBUTORS | xi |
| 1. CRYSTAL CHEMISTRY AND MAGNETIC STRUCTURES OF SUBSTITUTED $\text{Ca}_2\text{Fe}\text{O}_5$ | 1 |
| S. GELLER, R. W. GRANT and U. GONSER | |
| 2. STRUKTURCHEMIE EINIGER VERBINDUNGEN DER ÜBER- GANGSMETALLE MIT DEN ELEMENTEN C, Si, Ge, Sn | 27 |
| VON HANS NOWOTNY | |
| 3. LES BRONZES OXYGENES | 71 |
| PAUL HAGENMULLER | |
| 4. METALLIC OXIDES | 145 |
| JOHN B. GOODENOUGH | |
| 5. ELECTRONIC STRUCTURE, COLORATION AND PHOTODECOM- POSITION OF THE ALKALI-METAL AZIDES | 401 |
| D. A. YOUNG | |
| 6. DIPOLAR IMPURITIES IN ALKALI HALIDES: ZEEMAN AND STARK EFFECTS OF $\text{Sm}^{2+}:\text{K}^+$ VACANCY PAIR FLUORESCENCE, AND PARAELECTRIC RESONANCE AND RELAXATION OF OH^- IN KCl | 431 |
| L. A. VREDEVOE, C. R. CHILVER and F. K. FONG | |
| AUTHOR INDEX | 497 |
| CONTENTS OF PREVIOUS VOLUMES | 511 |



CRYSTAL CHEMISTRY AND MAGNETIC STRUCTURES OF SUBSTITUTED



S. GELLER, R. W. GRANT and U. GONSER

Science Center
North American Rockwell Corporation
Thousand Oaks, California

THE system $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$, being a constituent of Portland cement, has been of considerable interest and there have been many reports either on this system alone or as part of phase diagram work of broader scope. Only recently though has there been much interest in its magnetic behavior. The first application of linearly polarized recoil-free gamma rays to the solution of magnetic structure has been made successfully in studies of this system. Because previously, only a brief discussion of this technique was given, some further elaboration of it will be presented here. A section of this paper is devoted to a detailed discussion of the electric field gradient tensor in the $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$ system.

I. CRYSTAL CHEMISTRY

A brief review of some crystal chemical investigations of the $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$ system has been given most recently by Smith.⁽¹⁾ Hansen, Brownmiller and Bogue⁽²⁾ showed that aluminum could be substituted continuously for up to half the iron. McMurdie⁽³⁾ made a study of the $\text{CaO}-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3$ pseudoternary system in the region $\text{CaO}-4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3-\text{CaO} \cdot \text{Al}_2\text{O}_3$. In the area of our interest, McMurdie concluded that the $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 [\text{Ca}_2\text{AlFeO}_5]$ dissolves "between 3 and 5 percent of the calcium aluminates". Yamauchi⁽⁴⁾ gave as the maximum Al^{3+} ion content [the formula equivalent to] $\text{Ca}_2\text{Al}_{1.42}\text{Fe}_{0.65}\text{O}_{5.10}$ or $\text{Ca}_{1.96}\text{Al}_{1.39}\text{Fe}_{0.64}\text{O}_5$. This must only be an approximate formula, but the results of other investigations are quite close to $\text{Ca}_2\text{Al}_{1.36}\text{Fe}_{0.64}\text{O}_5$ for maximum Al^{3+} ion content.

Cirilli and Burdese⁽⁶⁾ reported that it is impossible to obtain a homogeneous phase with less than 20–21 wt. % Fe_2O_3 . The formula analogous to 21 wt. % is $\text{Ca}_2\text{Al}_{1.39}\text{Fe}_{0.61}\text{O}_5$. Malquori and Cirilli⁽⁷⁾ found a limiting composition of about

20.5 wt. % Fe_2O_3 and also reported obtaining single crystals of $\text{Ca}_2\text{Fe}_2\text{O}_5$, $\text{Ca}_2\text{AlFeO}_5$ and $\text{Ca}_2\text{Al}_{1.33}\text{Fe}_{0.67}\text{O}_5$ all of which appeared to be isostructural with brownmillerite. Toropov and Boikova⁽⁸⁾ claim that (1) $\text{Ca}_2\text{Al}_{1.5}\text{Fe}_{0.5}\text{O}_5$ and the members of the series of solid solutions between $\text{Ca}_2\text{Fe}_2\text{O}_5$ and $\text{Ca}_2\text{FeAlO}_5$ belong to the same structural type, but that (2) the composition $\text{Ca}_2\text{Al}_{1.33}\text{Fe}_{0.67}\text{O}_5$, which is said to be the limiting composition proposed by Swayze,⁽⁵⁾ does not have the same structure. However, there is ample evidence that both claims by Toropov and Boikova are not correct. Some of this evidence was later found by Boikova (herself) and Porai-Košic,⁽⁹⁾ who reported that the limiting composition is one with 22 wt. % Fe_2O_3 or $\text{Ca}_2\text{Al}_{1.36}\text{Fe}_{0.64}\text{O}_5$.

Newkirk and Thwaite⁽¹⁰⁾ reported that the solid solution range exists between $\text{Ca}_2\text{Fe}_2\text{O}_5$ and $\text{Ca}_{1.97}\text{Al}_{1.41}\text{Fe}_{0.61}\text{O}_5$. The latter composition is probably somewhat inexact. Smith reported work on single crystals with Al^{3+} content to $\text{Ca}_2\text{Al}_{1.34}\text{Fe}_{0.66}\text{O}_5$, but he did not attempt to determine the maximum Al^{3+} ion content.

The results outlined above indicate that the maximum attainable Al^{3+} content does not exceed that of the formula $\text{Ca}_2\text{Al}_{1.39}\text{Fe}_{0.61}\text{O}_5$ and may be somewhat lower as in $\text{Ca}_2\text{Al}_{1.36}\text{Fe}_{0.64}\text{O}_5$.

We mention that Midgley⁽¹¹⁾ has found from an examination of thirty-one different samples of Portland cement, the most frequently occurring composition of the subject phase present lay between $\text{Ca}_2\text{FeAlO}_5$ and $\text{Ca}_2\text{Al}_{0.67}\text{Fe}_{1.33}\text{O}_5$.

Thus far the most definitive work on the crystal structure of $\text{Ca}_2\text{Fe}_2\text{O}_5$ has been carried out by Bertaut, Blum and Sagnières⁽¹²⁾ (although Büssel⁽¹³⁾ first suggested the correct atomic arrangement of ions in brownmillerite $\text{Ca}_2\text{AlFeO}_5$, the structure of which is closely related to that of $\text{Ca}_2\text{Fe}_2\text{O}_5$). They found that $\text{Ca}_2\text{Fe}_2\text{O}_5$ belongs to space group $Pcnn-D_{2h}^{16}$ with $a = 5.64$, $b = 14.68$, $c = 5.39$ Å; $\rho_x = 4.06$ g cm⁻³, $Z = 4$. Projections of the structure (taken from the Bertaut *et al.* paper) down the a and c axes are shown in Fig. 1. The structure consists of alternate layers of FeO_6 octahedra sharing corners and FeO_4 tetrahedra sharing corners interleaved by Ca^{2+} ions surrounded by eight O^{2-} ions. Each octahedron shares two corners with tetrahedra in adjacent layers (Fig. 1). Octahedral Fe-O distances range from 1.96 to 1.97 Å, tetrahedral Fe-O distances from 1.86 to 1.87 Å, and Ca-O distances from 2.33 to 2.82 Å.

Gallagher, MacChesney and Buchanan⁽¹⁴⁾ have shown that $\text{Sr}_2\text{Fe}_2\text{O}_5$ and $\text{Ba}_2\text{Fe}_2\text{O}_5$ are isostructural with $\text{Ca}_2\text{Fe}_2\text{O}_5$ (although following Bertaut *et al.* they erroneously indicate them to be isostructural with brownmillerite—see later discussion). Additional oxidation of the iron ions to the tetravalent state increases the oxygen content of the unit cells and moves the structure toward that of a perovskite type. Watanabe *et al.*⁽¹⁵⁾ and Geller *et al.*⁽¹⁶⁾ have pointed out that the arrangement of all the cations and of the oxygen ions in the octahedra in $\text{Ca}_2\text{Fe}_2\text{O}_5$ is very similar to that in the perovskite-type structures.

The crystal structure of $\text{Ca}_2\text{Fe}_2\text{O}_5$ has undoubtedly been solved correctly by Bertaut *et al.*⁽¹²⁾ However, they also concluded that brownmillerite, $\text{Ca}_2\text{FeAlO}_5$, was isostructural with it, contrary to an earlier report by Büssel⁽¹³⁾ who had

content as found also by others. No discontinuity in lattice constant or in d_{141} and d_{202} spacings was observed. However, a change of slope occurs at about $x = 0.66$ for b , c and d_{202} vs. x . In fact, Newkirk and Thwaite⁽¹⁰⁾ had shown that the graphs of all lattice constants vs. composition showed linear decreases with increasing Al^{3+} ion content and changes in slope near the composition $\text{Ca}_2\text{Fe}_{1.34}\text{Al}_{0.66}\text{O}_5$. This is also indicative of a change in structure. The studies⁽¹⁷⁾ of magnetic structure (see below for details) with Mössbauer spectroscopy have confirmed the existence of two structures in the $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$ system. The room temperature phase boundary is in good agreement with Smith's estimate.

Smith⁽¹⁾ has also made an attempt to determine the distribution of Fe^{3+} and Al^{3+} ions over the octahedral and tetrahedral sites in the system $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$. The most convincing X-ray diffraction evidence for preferential substitution of Al^{3+} in the tetrahedral sites was given by the relative intensities of the $0k0$ reflections. Because in the transition from $Pcmn$ to $Icmm$, there is no change in y -parameters of the (Fe^{3+} , Al^{3+}) ions in both sites, and little change is expected in the y -parameters of the other ions, changes in the $0k0$, $k = 2n$, n odd, intensities should be particularly sensitive to changes in Al^{3+} ion concentration. (When $k = 4n$, the contributions from both sites have the same sign.) From this study as well as from steric considerations Smith suggests that the "Al atoms substitute preferentially for tetrahedrally-coordinated Fe atoms until about half the tetrahedral cations are Al. Then additional Al distributes itself nearly equally between the tetrahedral and octahedral sites. . . ." This is quite unlike what occurs when Al^{3+} is substituted for Fe^{3+} ion in the garnets, in which case after substitution of not more than 0.15 Al^{3+} ion per formula unit, Al^{3+} begins to enter octahedral sites but continues to prefer the tetrahedral sites.⁽¹⁸⁾ The results of Mössbauer spectroscopy prove that in the $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$ system, the beginning of Al^{3+} entry into octahedral sites occurs at lower than 0.5 Al^{3+} ion content (per formula unit). The distribution of the aluminum in $\text{Ca}_2\text{Fe}_{1.5}\text{Al}_{0.5}\text{O}_5$, quenched from 1225°C is given by the formula $\text{Ca}_2[\text{Fe}_{0.90}\text{Al}_{0.10}](\text{Fe}_{0.60}\text{Al}_{0.40})\text{O}_5$,⁽¹⁷⁾ where [] and () indicate octahedral and tetrahedral sites respectively. Brownmillerite, $\text{Ca}_2\text{FeAlO}_5$, is suggested by Smith to have the approximate distribution as given in the formula $\text{Ca}_2[\text{Fe}_{0.75}\text{Al}_{0.25}](\text{Fe}_{0.25}\text{Al}_{0.75})\text{O}_5$; the distribution found by Mössbauer spectroscopy⁽¹⁹⁾ for a specimen quenched from 1290°C is $\text{Ca}_2[\text{Fe}_{0.68}\text{Al}_{0.32}](\text{Fe}_{0.32}\text{Al}_{0.68})\text{O}_5$. (See also Fig. 2.)

Prior to the result reported by Geller, Grant and Fullmer,⁽¹⁷⁾ Pobell and Wittman⁽²⁰⁾ confirmed qualitatively Smith's results on $\text{Ca}_2\text{FeAlO}_5$, that is, that the Al^{3+} ions prefer the tetrahedral sites, but a substantial amount of Al^{3+} ions enter octahedral sites.

Several other ions, Sc^{3+} , Ga^{3+} and Cr^{3+} , have been substituted for Fe^{3+} in $\text{Ca}_2\text{Fe}_2\text{O}_5$. In the Cr^{3+} case,⁽²¹⁾ substitution to $x = 0.5$ has been made with no change in magnetic structure from that of $\text{Ca}_2\text{Fe}_2\text{O}_5$. (Only an abstract has been written on this work.) It is very likely that all the Cr^{3+} ions enter the octahedral sites.

Within experimental error, for Sc^{3+} substitution all the Sc^{3+} ions enter octahedral sites: the measured value for a total substitution of 0.50 Sc^{3+} ion per formula unit is actually 0.47 ± 0.04 , determined from analysis of the Mössbauer hyperfine patterns.⁽²²⁾ The fraction of tetrahedral sites occupied by Ga^{3+} , C_t , is plotted against x in Fig. 2. While the point for $x = 2.00$ is fictitious, if $\text{Ca}_2\text{Ga}_2\text{O}_5$ had the $\text{Ca}_2\text{Fe}_2\text{O}_5$ structure, C_t for it must be 1.0.

In the cases of Sc^{3+} and Ga^{3+} ion substitution the exact maximum amounts possible were not determined, although they are close to $x = 0.50$ and 1.50 respectively. For values of x less than these, the phases are isostructural with $\text{Ca}_2\text{Fe}_2\text{O}_5$. Thus, as far as is presently known, only the substitution of Al^{3+} causes the structural change from the $Pcmn$ to the $Icmm$ space group. Inasmuch

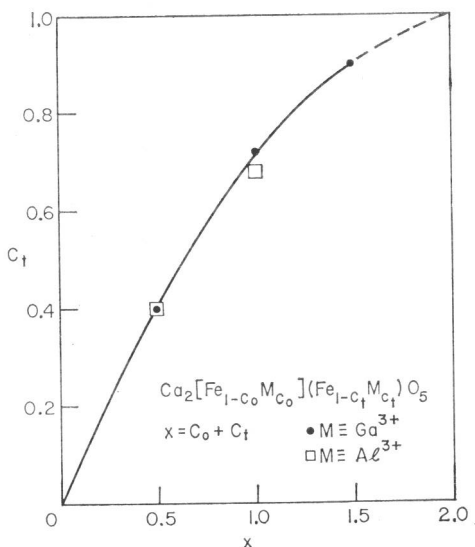


FIG. 2. Fraction, C_t , of tetrahedral sites occupied by Al^{3+} or Ga^{3+} ions.

as only ions with spherical (or pseudospherical) electronic configurations are involved it would appear that indeed (see ref. 1) the very small size of the Al^{3+} ion is the main cause of this structural change.

The determination of the distribution of diamagnetic ions over the two crystallographically nonequivalent sites leads to an estimate of the enthalpy difference for these ions in the two sites.⁽²²⁾ Considering only contributions to the configurational entropy, and denoting the fractions, C_0 and C_t , of the octahedral and tetrahedral sites occupied by diamagnetic ions, we have

$$\exp [(H_t - H_0)/kT] = (1 - C_t)C_0/(1 - C_0)C_t$$

where $H_t - H_0$ is the enthalpy difference for a diamagnetic ion occupying the two sites. The Ga^{3+} and Sc^{3+} ion substituted specimens were quenched from

$\sim 1170^\circ\text{C}$, giving $(H_t - H_0)$ of -0.23 ± 0.04 eV independent of x for Ga^{3+} and > 0.29 eV for Sc^{3+} at 0.5. The value for Sc^{3+} is only a lower limit; because $C_t (= 0.03 \pm 0.04)$ is small the true value of $H_t - H_0$ could be appreciably larger. For Al^{3+} ion substitutions and a quench temperature of 1250°C , a value of $H_t - H_0 = -0.18 \pm 0.03$ eV is consistent with the data.

II. MAGNETIC STRUCTURES

The first prediction of the spin arrangement in $\text{Ca}_2\text{Fe}\text{O}_5$ was made from crystal chemical considerations.⁽¹⁶⁾ The ideas used were rather simple. First, because $\text{Sr}_2\text{Fe}\text{O}_5$ had a high Néel temperature ($> 600^\circ\text{K}$),⁽¹⁴⁾ it

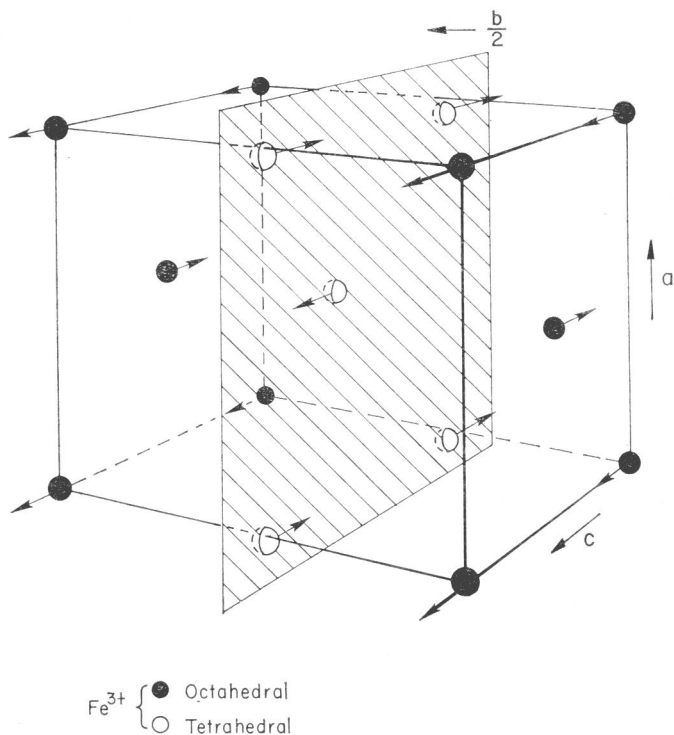


FIG. 3. Spin arrangement and directions in $\text{Ca}_2\text{Fe}_2\text{O}_5$.

could be assumed that this would certainly be true of isostructural $\text{Ca}_2\text{Fe}\text{O}_5$, which was easier to deal with chemically. Also, it could be seen, even with a small permanent magnet, and without making quantitative measurements, that the susceptibility was low† even at liquid N_2 temperature, implying strong

† Measurements by Malquori and Cirilli⁽⁷⁾ in the $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$ system at room temperature show low susceptibilities, essentially independent of applied field in the range 1500–2460 Oe.

superexchange interactions. This, of course, is consistent with the high Néel temperature (see, for example, ref. 23 and pertinent references therein). Second, substitution of Ga^{3+} ions with expected tetrahedral site preference, or Sc^{3+} ions with expected octahedral site preference did not produce a noticeable spontaneous moment, thus implying⁽²⁴⁾ that $\text{Ca}_2\text{Fe}\text{O}_5$ was not a compensated ferrimagnet. These observations led to the prediction that each sublattice is antiferromagnetic and that the intersublattice interactions are also antiferromagnetic. Because the arrangement of the cations and of the oxygen ions in the octahedra is very similar to that in the perovskite, it was predicted that the spin arrangement would be essentially that of the Koehler and Wollan type G structure of LaFeO_3 . (Since the earlier work of Koehler and Wollan,⁽²⁵⁾ much attention has been given to the magnetic structures of the rare earth iron perovskites and refinements have been made.⁽²⁶⁾ However, the Fe^{3+} ion spin arrangement in LaFeO_3 and others is essentially that of type G.)

Mössbauer spectroscopy confirmed the expected site preferences of the Sc^{3+} and Ga^{3+} ions.⁽¹⁶⁾ Subsequently, the spin directions were determined with the use of linearly polarized recoil-free γ -rays⁽²⁷⁾ (see last section). The spins lie in a plane perpendicular to the orthorhombic b -axis and parallel to the c -axis (Fig. 3). The magnetic space group, to which the structure belongs^(28,19) is $Pcm'n'$. This magnetic space group does permit a ferromagnetic component along the a -axis. Even without a quantitative measurement, it could be readily seen that such a moment must be substantially smaller than that of YFeO_3 which, at room temperature, has about $0.05 \mu_B/\text{formula unit}$.⁽²⁹⁾

At about the same time that the work on $\text{Ca}_2\text{Fe}_2\text{O}_5^\dagger$ by Geller *et al.*⁽¹⁶⁾ was in progress, Corliss *et al.*⁽²¹⁾ were working on the $\text{Ca}_2\text{Fe}_{2-x}\text{Cr}_x\text{O}_5$ system with neutron diffraction. Their results confirm the structure found by the crystal-chemical and Mössbauer techniques. Another neutron diffraction study was carried out by Friedman *et al.*,⁽²⁸⁾ also confirming the previously obtained results. Friedman *et al.*⁽²⁸⁾ were the first to report the magnetic space group, although, based on the assumption that the chemical and magnetic cells remained the same, it was readily derivable after the spin directions were found by the use of linearly polarized γ -rays.⁽²⁷⁾

Still another neutron diffraction investigation of $\text{Ca}_2\text{Fe}_2\text{O}_5$ was carried out by Takeda *et al.*⁽³²⁾ who also confirmed the structure suggested by the crystal-

[†] In a paper⁽³⁰⁾ published over a year after the Geller *et al.* paper⁽¹⁶⁾ on the spin arrangement in $\text{Ca}_2\text{Fe}\text{O}_5$, Whitfield reported results of Mössbauer spectroscopy on the $\text{Ca}_2\text{Fe}_5\text{O}_5\text{-CaFeAlO}_5$ system. The work appeared to have been done independently even though the Geller *et al.*⁽¹⁶⁾ and Pobell-Wittmann⁽²⁰⁾ papers had appeared substantially earlier. The conclusions at which Whitfield arrived were quite similar to those of Geller *et al.* as regards spin arrangement. However, he indicated the probable existence of two Néel temperatures in $\text{Ca}_2\text{Fe}_2\text{O}_5$ associated with ordering in the octahedral and tetrahedral sites. Such a hypothesis was not justifiable and this is adequately discussed in a subsequent publication by Geller *et al.*⁽³¹⁾

chemical and Mössbauer spectroscopic investigations. In a footnote in their paper they point out that a preliminary part of their study was cited by Hirone⁽¹⁵⁾ in 1965. The Hirone paper covered several investigations then going on at the Research Institute for Iron, Steel and Other Metals in Tokyo and consequently gave very little attention to the work on $\text{Ca}_2\text{Fe}_2\text{O}_5$. Unfortunately, all subsequent investigators missed this reference.

The preliminary part was the report that Watanabe, Sugimoto and Fukase had found the existence of weak ferromagnetism in $\text{Ca}_2\text{Fe}_2\text{O}_5$ below $\approx 400^\circ\text{C}$ (the approximate Néel temperature). They recognized that the $\text{Ca}_2\text{Fe}_2\text{O}_5$ structure is derivable from the perovskite and concluded that the magnetic structure was of the G type (of Koehler and Wollan). However, while they arrived at the right conclusion, it is necessary to point out that their evidence was inadequate to make it. They argue that based on symmetry considerations, weak parasitic ferromagnetism from both sublattices "is possible in *c*-direction if the spin axis lie in *a*-direction and vice versa". The magnetic space groups derivable directly from *Pcmn* permit either an essentially G-type magnetic structure or a compensated ferrimagnet. In the compensated ferrimagnet the individual sublattices would be ferromagnetic.† In the subsequent paper by Takeda *et al.*, they again indicate that the G-type structure is derivable uniquely from the $\text{Ca}_2\text{Fe}_2\text{O}_5$ crystal structure. However, this is not so, mainly because the two Fe^{3+} sublattices are crystallographically nonequivalent.

It is worth emphasizing that all work on $\text{Ca}_2\text{Fe}_2\text{O}_5$ subsequent to the magnetic structure determination by the combination of crystal chemical and Mössbauer spectroscopic techniques confirmed the conclusions of that work. Thus, this combination offers powerful tools for determination of simple magnetic structures. Mössbauer spectroscopy on single crystals with and without applied fields can in itself lead to magnetic structure determination, but as shown by Geller *et al.*,⁽¹⁶⁾ the crystal chemical approach can, also by itself, lead to important conclusions regarding spin arrangement and put limitations on spin directions. Together, the two techniques complement each other.

No neutron diffraction results have as yet been reported on the magnetic structure of the *Icmm* phases although the magnetic structure has been deduced from linearly polarized γ -ray spectroscopy of single crystals.⁽¹⁹⁾ Because the materials, $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$, $x > 0.66$, also have low susceptibility, and high Néel temperatures, the individual magnetic sublattices must both be antiferromagnetic. The magnetic space groups directly derivable from *Icmm* restrict the spins on octahedral sites to lie parallel or perpendicular to the *c*-axis, while those on the tetrahedral sites may be parallel to *a*, *b*, or *c*. The plots of lattice constant versus composition show that there is no abrupt switch in the *a*- and *c*-axes;⁽¹⁰⁾ that is, the orientation is the same in both space groups. Figure 4, taken from

† The spin moments in the two sublattices could be aligned in the same direction, in which case the crystals would be ferromagnetic.

Smith's paper⁽¹⁾ is a stereoscopic pair of the $\text{Ca}_2\text{Fe}_2\text{O}_5$ structure and shows how it is expected to move into the $Icmm$ or brownmillerite structure.

By applying the same technique as was used for the determination of spin directions in $\text{Ca}_2\text{Fe}_2\text{O}_5$, it was found⁽¹⁹⁾ that in $\text{Ca}_2\text{FeAlO}_5$, the spins are directed along the a -axis (to within $\approx 10^\circ$, experimental error). The most probable magnetic space group is $Ic'm'm'$, which requires the tetrahedral site spins to be *exactly* along a , but permits the octahedral spins to be slightly tilted in the ab -plane. Such tilting, if it exists, must be less than 10° , which is the experimental error of the results of the Mössbauer spectroscopy (see below). However, unlike the case of $\text{Ca}_2\text{Fe}_2\text{O}_5$ which belongs to $Pcm'n'$ and has a slight ferromagnetic component,⁽³²⁾ $\text{Ca}_2\text{FeAlO}_5$ (and isostructural solid solutions) should be purely antiferromagnetic because $Ic'm'm'$ does not permit weak ferromagnetism.

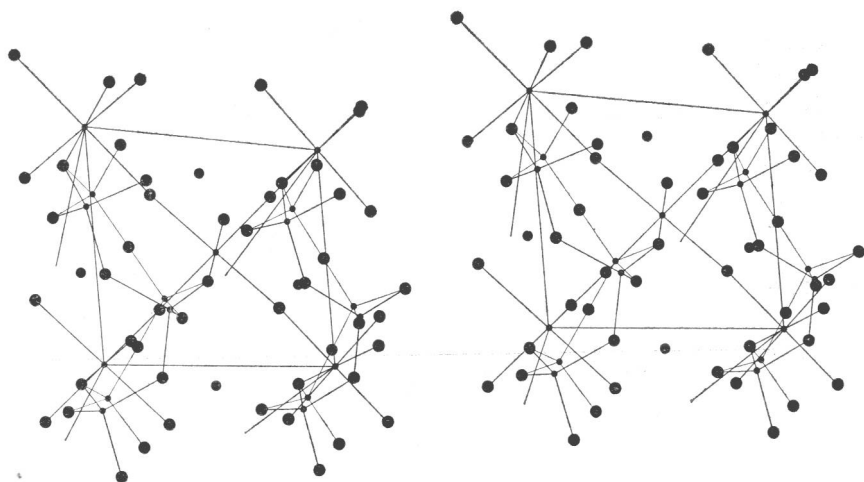


FIG. 4. Stereoscopic pair showing half the unit cell in the structure of $\text{Ca}_2\text{Fe}\text{O}_5$ as determined by Bertaut *et al.*⁽¹²⁾ viewed approximately along the b -axis. The atoms connected by the lighter lines indicate the proposed structural change from the $Pcmn$ to $Icmm$ space group. Fe and Al sites are indicated by small closed circles, oxygen sites by large closed circles, and Ca sites by intermediate size closed circles without bonds. From ref. 1.

In the T vs. x diagram of the $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$ system, there is a region (Fig. 5) in which two magnetic phases coexist.⁽¹⁷⁾ The amounts of each phase for given x appear to be a reversible function of temperature. The observations were made on single crystals with the linearly polarized γ -ray technique. While there are alternate interpretations,⁽¹⁷⁾ it is felt presently that the spin direction (that is, either along c or a) indicates which structure exists, i.e. either that of $Pcm'n'$ or that of $Ic'm'm'$. In an equilibrium diagram the region may coalesce into a line,