Magnetic Structure of $Ca_2Fe_2O_5$

Takayoshi TAKEDA, Yasuo YAMAGUCHI and Shoichi TOMIYOSHI

The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai

Masahiro FUKASE

Konishiroku Photo Industries Company Limited, Hino, Tokyo

Mitsuo SUGIMOTO

The Institute for Physical and Chemical Research, Komagome, Tokyo

and

Hiroshi WATANABE

The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai

and

The Institute for Physical and Chemical Research, Komagome, Tokyo

(Received September 14, 1967)

Magnetic measurements indicate that $Ca_2Fe_2O_5$ is an antiferromagnet, with weak parasitic ferromagnetism. The lattice, with the space group $Pcmn\text{-}D_{2h}^{16}$, can be considered as an oxygen deficient perovskite. The magnetic structure as determined from a neutron diffraction study is of G-type, and Fe^{3+} spins are directed approximately along c-axis.

§1. Introduction

The crystal structure of $Ca_2Fe_2O_5$ has been studied by Bertaut *et al.*.[1,2] It is orthorhombic and the space group is $Pcmn\text{-}D_{2h}^{16}$. The lattice constants, according to these authors, are: $a=5.64$, $b=14.68$ and $c=5.39$ Å. Subsequently Smith[3] confirmed Bertaut *et al.*'s results.

There are two types of iron sites, Fe_I and Fe_{II}, which alternate along the b-axis. Fe_I is an octahedral site surrounded by 6 O^{2-}, while Fe_{II} is a tetrahedral site surrounded by 4 O^{2-} ions. The crystal lattice can be regarded as a deformed, oxygen-deficient perovskite. The unit cell of this lattice is made up of four unit cells of primitive perovskite cells stacked in the b-direction.* Hence the magnetic structure of this antiferromagnetic compound has been considered as of G-type, on the analogy of the magnetic structure usually met with in Fe^{3+} containing perovskite oxides. In G-type structure, near-neighboring Fe^{3+} ions have always opposite spins. Then the two sublattices, Fe_I and Fe_{II}, are antiferromagnetic within each of them as well as to each other. (Fig. 1)

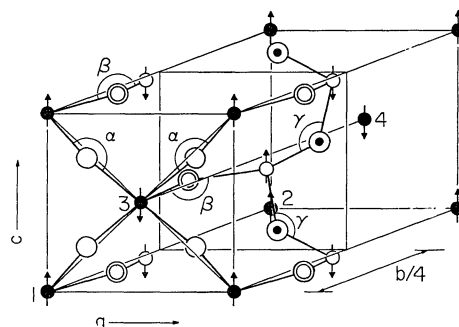Geller *et al.*[5] studied the Fe^{57} Mössbauer effect

---

* The preliminary part of the present study (Watanabe, Sugimoto and Fukase) was cited by Hirone,[4] at the Conference on Magnetism and Magnetic Materials, Minneapolis, 1964. Two errata, however, should be mentioned: "c-axis" should read "b-axis", and "stacked in c-direction" should read "stacked in b-direction".

Fig. 1. Crystal structure and proposed magnetic structure of $Ca_2Fe_2O_5$.

$a=5.64$, $b=14.68$ and $c=5.39$ Å.

● Fe_I	○ O_I	$(b=0)$
◎ O_{II}		$(b=0.133)$
○ Fe_{II}	⊙ O_{III}	$(b=1/4)$

Center of inversion at Fe_I, and mirror plane at $b=1/4$.

$\alpha=167°$	$Fe_I\text{-}O_I$	1.96_8 Å
$\beta=147°$	$Fe_I\text{-}O_{II}$	1.97_7 Å
$\gamma=132°$	$Fe_{II}\text{-}O_{II}$	1.88_4 Å
	$Fe_{II}\text{-}O_{III}$	1.85_8 Å and 1.85_9 Å

of $Ca_2Fe_2O_5$ and of compounds in which Fe^{3+} are partially replaced by Ga^{3+} or Sc^{3+}. These ions were expected, and actually found, to go into one of the two sublattices preferentially (Ga^{3+} to Fe_{II}, and Sc^{3+} to Fe_I), so that it was expected that the substituted compound should become ferrimagnetic if each of the sublattices had nonzero moment. But since this was not the case, they concluded that the magnetic structure was of

G-type, as has been expected above. In a subsequent study of the Mössbauer effect with linearly polarized γ rays, Gonser et al.[6] suggested that the spin direction was along the *c*-axis.

In order to ascertain these considerations, a neutron diffraction experiment was performed with the TOG neutron diffractometer at JRR-3. The spin direction was investigated as well as the antiferromagnetic structure. On the basis of the proposed structure, occurrence of weak parasitic ferromagnetism was expected. This was borne out by a thermomagnetic study.

§ 2. Neutron Diffraction Study

Powdered samples were sintered from constituent compounds, $CaCO_3$ and Fe_2O_3, at about 1200°C in air for 3 hrs, and then annealed at 1150°C for 3 hrs. Small amounts of ferromagnetic impurities, if any, were removed by this annealing process. *X*-ray diffraction pattern was taken, and it was found that both line positions and line intensities were in complete conformity with Bertaut et al.'s.[1,2] Neutron diffraction patterns were taken with TOG neutron diffractometer installed at JRR-3 of JAERI. The pattern taken at liquid nitrogen temperature is shown in Fig. 2. All the existing lines could be indexed on the basis of the chemical unit cell, except for some amount of contamination with Al, mainly from the aluminum sample holder. Observed magnetic intensity was deduced from the difference pattern between the liquid nitrogen temperature run and
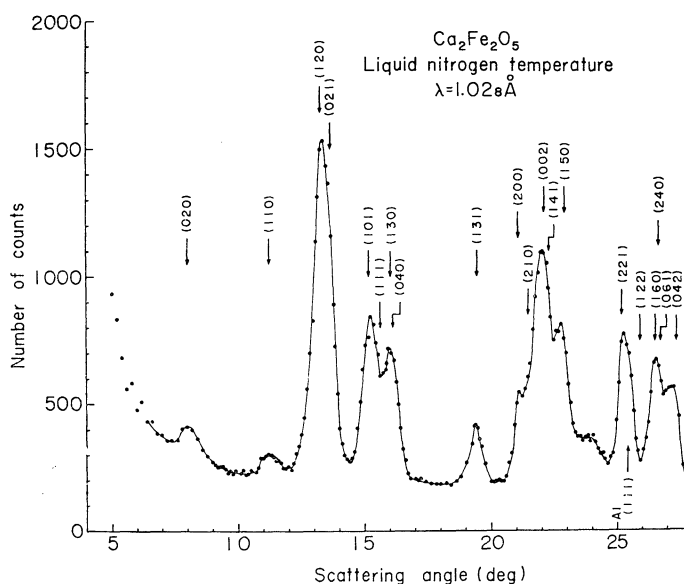

Fig. 2. Neutron diffraction pattern of $Ca_2Fe_2O_5$ at liquid nitrogen temperature.

a run taken at 480°C. Theoretical intensity was calculated using the atomic parameters given by Bertaut et al.[2] and with the aid of NEAC 2230 computer at Tohoku University, and the form factor of Mn^{2+} by Shull, Strauser and Wollan[7] was used. In Table I comparison between observed and calculated intensities is given on the basis of the *G*-type antiferromagnetic structure. Here the Fe^{3+} spins are assumed to be directed along *c*-axis. For other posibilties we will discuss later on. Because of the large lattice constants, most of the peaks consist of a number of lines which are not separable. For the determination of the scale value, we have chosen the peak including the line (101) as the reference, since this peak contains fairly strong nuclear intensity and relatively small magnetic intensity. Agreement between observed and calculated intensities is on the whole good. Although the Mössbauer effect measurements by Geller et al.[5] and Gonser et al.[6] showed that the internal fields for the two crystallographic sites (4*a* and 4*c*) were different, it was suspected that the Fe^{3+} moments had the same value. In order to check this point, we sought (100) peak carefully, without finding any intensity. So within the experimental error, Fe^{3+} moments could be assumed to be the same for the different crystallographic sites. They were found to be 4.5 ± 0.2 μ_B.

Although the *G*-type antiferromagnetic struc-

Table I. Comparison between observed and calculated intensties of the powder neutron diffraction data of $Ca_2Fe_2O_5$ taken at liquid nitrogen temperature. Fe^{3+} atomic moments are assumed to be equal to 4.54 μ_B for both of the crystallographic sites. For the model for theoretical intensity, see text. Fe^{3+} moments are assumed to be along c-axis.

khl (Pcmn)	2θ (deg)	Theoretical intensity Nuc.		Mag.		Total	Experimental intensity Nuc.	Mag.	Total
020	8.03	13.15	13.15	0	0	13.15	12.2	0	12.2
100	10.46	0		0.28					
110	11.20	11.63	11.63	0	0.86	12.49	11.9	0	11.9
011	11.66	0		0.59					
120	13.20	0	0	118.03	158.32	158.32	0	158.3	158.3
021	13.59	0		40.28					
101	15.16	50.66		0.24					
111	15.68	7.56		3.76					
130	15.98	15.38	94.37	0	5.63	100.00			100
040	16.10	19.81		0					
031	16.31	0		1.20					
121	17.18	0.96		0.44					
140	19.24	0		0.13					
131	19.41	9.99	9.99	2.73	2.88	12.87	11.1	4.8	15.9
041	19.51	0		0.03					
200	21.00	24.34		0					
210	21.39	0		5.60					
002	21.99	38.18		0					
141	22.18	33.77		0.26					
012	22.36	0.40		0					
220	22.52	3.65		0					
150	22.76	29.28		0					
051	23.00	0	142.93	0.63	12.28	155.21	149.6	18.9	168.5
022	23.44	8.83		0					
201	23.74	3.63		0.88					
211	24.08	0.07		0.43					
060	24.25	0.30		0					
230	24.28	0		3.74					
102	24.40	0.34		0.10					
112	24.74	0.13		0.65					
221	25.10	5.55		21.80					
032	25.15	0.22	11.01	0	30.73	41.73	11.8	31.0	48.9
151	25.32	4.88		1.44					
122	25.73	0.35		7.49					
111 (Al)	25.40						6.1		
160	26.48	0		15.85					
240	26.58	13.12		0					
061	26.68	0	42.71	13.49	30.58	73.29	39.9	27.3	67.4
231	26.71	2.18		0.32					
132	27.30	16.29		0.92					
042	27.37	11.12		0					

ture is certainly reasonable both from the standpoint of the crystallographic nature of this substance as well as from its compatibility with the neutron diffraction data, a ferrimagnetic model was also tested in which Fe_I and Fe_{II} moments point in the opposite directions. For this model the structure factor is

$$S = 4f(Fe_I) - 4f(Fe_{II})(-1)^{k/2} \cos 2\pi hx \cos 2\pi lz$$

for $h+l$ even and k even, and

$$S = 4f(Fe_{II})(-1)^{k/2} \sin 2\pi hx \sin 2\pi lz$$

for $h+l$ odd and k even. The former examples are:

$$(020): \quad S = 4(f(Fe_I) + f(Fe_{II})) ,$$

and

$$(121): \quad S = 4f(Fe_I) + 3.385 f(Fe_{II}) .$$

The latter examples are:

$$(120): \quad S = 1.748 f(Fe_{II})$$

and

$$(021): \quad S = 1.355 f(Fe_{II}) .$$

Hence there should be big magnetic intensities in (020) and (121), while (120) and (021) magnetic intensities should not be so large. The actually

Table II. Calculated Intensity of the powder diffraction data of $Ca_2Fe_2O_5$ taken at liquid nitrogen temperature. Fe^{3+} moments are assumed to be along a or b direction. Calculations are based on the G-type antiferromagnetic model.

hkl	Intenstiy (Nuc. +Mag.)		Experimental intensity
	S_a $\mu=4.55$ μ_B	S_b $\mu=4.78$ μ_B	
120	44.29 ⎱ 158.32	78.86 ⎱ 158.32	158.3
021	114.03 ⎰	79.47 ⎰	
101	50.23	49.12	
111	11.49	14.55	
130	15.16	14.74	
040	19.54 ⎬ 100.00	19.00 ⎬ 100.00	100.0
031	2.17	1.05	
121	1.40	1.53	
221	13.39	32.60	
032	0.22 ⎬ 43.46	0.21 ⎬ 65.46	48.9
151	6.25	5.36	
122	23.60	27.29	
160	13.21	2.66	
240	12.94	12.58	
061	16.12 ⎬ 73.83	2.95 ⎬ 49.15	67.4
231	2.29	2.41	
132	18.30	17.88	
042	10.97	10.67	

observed intensities, however, are in violent disagreement with this situation, so that the ferrimagnetic model is apparently improbable.

The spin direction is more difficult to determine. In Table II we have shown the result of calculation similar to that given in Table I, but the spin direction is assumed to be along a or b axis. Spin//a is more consistent with experiment than spin//b, since in the latter case the calculated intensity for the peak including (221) line is too strong, while that including (160) is too small. Then we have to compare spin//a with spin//c. The compatibilities of these two models with experiment are about the same. So we decided to measure the shape of the (120)+(021) peak carefully, in order to choose a better one out of them. As can be seen from the tables, (120) intensity is bigger than (021) intensity for spin//c, and the situation is reversed for spin//a. The measurement was done at room temperature with the sample in a cassette with a smaller diameter (15 mm) and with a higher counting statistics. This was meant to increase the resolution. Actually we could obtain an asymmetrical shape of the peak as shown in Fig. 3. The data show that spin//c is more favorable.

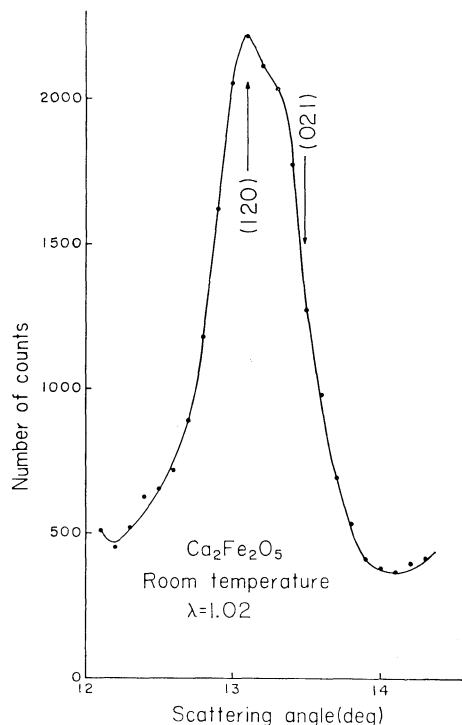The above conclusion of the spin direction is in

Fig. 3. Line profile of the (120)+(021) peak at room temperature.

accord with that of the polarized Mössbauer data by Gonser *et al.*.[6] In the course of preparing the manuscript, we have become aware of an abstract of Corliss *et al.*'s neutron work[8] who reported the same result as above. Their moment value, 4.4 μ_B, is also fairly close to ours.

The temperature dependence of the (120)+(021) peak intensity was measured up to the Néel temperature, T_N. This is shown in Fig. 4. T_N
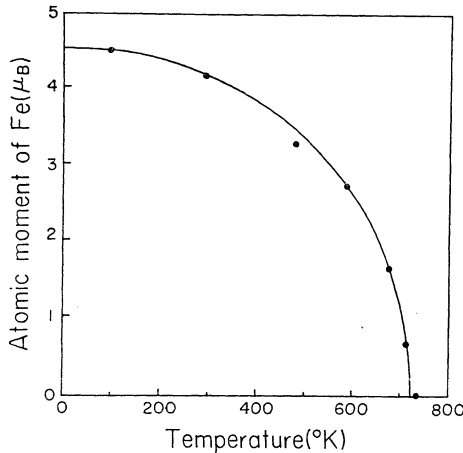

Fig. 4. Temperature dependence of the Fe^{3+} atomic moment as deduced from the (120)+(021) peak intensity.

=720°K in the present experiment, as compared to 730°K by Corliss *et al.*.[8] The curve in the figure is a Brillouin fit to the experimental points, with spin 5/2.

§ 3. Magnetic Study

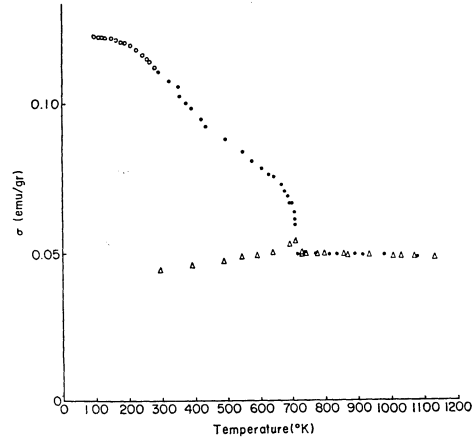As stated above, $Ca_2Fe_2O_5$ is an antiferromagnetic with $T_N=720°K$. Its thermomagnetic curve, however, shows that it has a thermorema-

Fig. 5. Thermomagnetic curve of $Ca_2Fe_2O_5$ under the field of $H=3950$ Oe, △ experimental point measured during heating. ● and ○ experimental points measured during cooling under a magnetic field.

nent magnetization if it is cooled from above T_N under a magnetic field. In Fig. 5, one can see the magnetization during cooling under a magnetic field is by far greater than that during heating. After this treatment the magnetization (hysteresis curve) is shifted along *the magnetization axis*. The phenomenon is much the same as has been observed in many orthoferrites with the perovskite-type structure.[9] This anomalous shift is due to an extremely large coercive force brought about by the smallness of the net magnetization.

The origin of the weak ferromagnetism is considered to be the Dzyaloshinskii-Moriya interaction.[10] Consideration of the symmetry elements leads to the following relation between the spin components S_i (for numbering of spins, see Fig. 1):

$$S_{1x}^{(2)}=\varepsilon S_{1x}^{(1)} , \quad S_{1y}^{(2)}=-\varepsilon S_{1y}^{(1)} , \quad S_{1z}^{(2)}=\varepsilon S_{1z}^{(1)} ,$$
$$S_{1x}^{(3)}=-\varepsilon' S_{1x}^{(1)} , \quad S_{1y}^{(3)}=\varepsilon' S_{1y}^{(1)} , \quad S_{1z}^{(3)}=\varepsilon' S_{1z}^{(1)} ,$$
$$S_{1x}^{(4)}=-\varepsilon\varepsilon' S_{1x}^{(1)} , \quad S_{1y}^{(4)}=-\varepsilon\varepsilon' S_{1y}^{(1)} , \quad S_{1z}^{(4)}=\varepsilon\varepsilon' S_{1z}^{(1)} , \tag{1}$$

where ε and ε' take the values ±1. The components of the net moment vector

$$m_I=S_I^{(1)}+S_I^{(2)}+S_I^{(3)}+S_I^{(4)}$$

can be written as:

$$m_{Ix}=(1+\varepsilon)(1-\varepsilon')S_{Ix}^{(1)} ,$$
$$m_{Iy}=(1-\varepsilon)(1+\varepsilon')S_{Iy}^{(1)} , \tag{2}$$
$$m_{Iz}=(1+\varepsilon)(1+\varepsilon')S_{Iz}^{(1)} .$$

As the magnetic structure is of *G*-type, $S_I^{(1)} \sim S_I^{(2)} \sim -S_I^{(3)} \sim -S_I^{(4)}$, so that the vector

$$l_I=S_I^{(1)}+S_I^{(2)}-S_I^{(3)}-S_I^{(4)}$$

should have a non-zero absolute value. From (1) it follows that:

$$l_{Ix}=(1+\varepsilon)(1+\varepsilon')S_{Ix} ,$$
$$l_{Iy}=(1-\varepsilon)(1-\varepsilon')S_{Iy} , \tag{3}$$
$$l_{Iz}=(1+\varepsilon)(1-\varepsilon')S_{Iz} .$$

The case $\varepsilon=-1$, $\varepsilon'=+1$ is inhibited, bacause, then, all of the components of l in (3) vanish. Hence we have three cases:

(1) $\varepsilon = \varepsilon' = +1$.

From (3) we have $l_{Ix} = 4S_{Ix}$ and $l_{Iy} = l_{Iz} = 0$ so that the approximate spin direction is along the a-axis. From (2) $m_{Ix} = m_{Iy} = 0$, $m_{Iz} = 4S_{Iz}$ and a small moment appears in the c-direction.

(2) $\varepsilon = 1, \varepsilon' = -1$.

$l_{Ix} = l_{Iy} = 0$, $l_{Iz} = 4S_{Iz}$, so that the approximate spin direction is along the c-axis. From (2) $m_{Ix} = 4S_{Ix}$, $m_{Iy} = m_{Iz} = 0$ and a small moment appears in the a-direction

(3) $\varepsilon = \varepsilon' = -1$

$l_{Ix} = l_{Iz} = 0$, $l_{Iy} = 4S_{Iy}$, so that the approximate spin direction is along the b-axis. From (2) $m_{Ix} = m_{Iy} = m_{Iz} = 0$ and no net moment appears. The same argument holds for Fe_{II} spins.

The neutron diffraction result is consistent with this consideration, case (2) being realized.

§ 4. Relation to the Mössbauer Effect Studies

As stated above, the result that the spins are directed along the c-axis is consistent with the Mössbauer effect measurement by Gonser et al..[6] It is interesting now to compare the observed quadrupole interaction with the calculated value on the basis of the established spin direction.

Gonser et al.'s[6] data on polycrystalline samples showed that the quadrupole interaction in $Ca_2Fe_2O_5$ is negative for octahedral (Fe_I) sites, while it is positive for tetrahedral (Fe_{II}) sites. This has been confirmed by Wittmann et al..[11] On the other hand, an electronic computer calculation has been made of the electric field gradient tensor for each site of Fe by Wittmann[12] and by Hudson et al.,[13] independently. Both the Fe atoms have been considered to be in the Fe^{3+} state, which is spherically symmetric. Therefore the calculation has been made on the assumption that the major contribution to the quadrupole interaction was the field gradient due to the surrounding atoms. The results of the calculation by these two authors coincided with each other, as they should, except for detailed figures. The calculated q_z (or the electric field gradient along c-axis) for both sites were positive. Now to the 0th through 2nd order perturbation theory of the hyperfine interaction the difference of the separations of the peaks

$$(6-5)-(2-1) = 4\Delta E$$

is related to q_z by the following formula:

$$4\Delta E = eQq_z , \qquad (4)$$

Q being the quadrupole moment of the Fe^{57} nucleus and e the electronic charge.[14] The

relation (4) is modified if the 3rd and 4th order perturbations are taken into account,[15] but the effect is small in the present case, and can be neglected. The result of the calculation that the value of q_z for Fe_I is positive is therefore in disagreement with that of the experiment that ΔE for Fe_I is negative.

The reason for the disagreement may be considered as partly due to the point change approximation and partly to negligence of the covalent character of Fe ions. The internal fields for Fe(I) and Fe(II) sites are 555 and 505 kOe at $0°K$[11] or 534 and 467 kOe at $5°K$,[12] respectively. These values are considerably lower than those found in compounds with completely ionic character, eg FeF_3, whose internal field is 622 kOe at $4°K$.[16] Also the atomic moment of Fe found in $Ca_2Fe_2O_5$ in the present study, 4.5 μ_B, is lower than the Fe^{3+} value of 5 μ_B. These may be regarded as indications that the compound is not purely ionic.

After completion of the present manuscript, a paper on the neutron diffraction study on $Ca_2Fe_2O_5$ by Friedman et al.[17] has appeared. Their conclusion on the magnetic structure is the same as ours.

References

1) E. F. Bertaut, P. Blum et G. Magnano: CR Acad. Sci. **244** (1957) 2944.
2) E. F. Bertaut, P. Blum et A. Sagnières: Acta cryst. **12** (1959) 149.
3) D. K. Smith: Acta cryst. **15** (1962) 1146.
4) T. Hirone: J. appl. Phys. **36** Part 2 (1965) 988.
5) S. Geller, R. W. Grant, U. Gonser, H. Wiedersich and G. P. Espinosa: Phys. Letters **20** (1966) 115.
6) U. Gonser, R. W. Grant, H. Wiedersich and S. Geller: Appl. Phys. Letters **9** (1966) 18.
7) C. G. Shull, W. A. Strauser and E. O. Wollan: Phys. Rev. **83** (1951) 333.
8) L. M. Corliss, J. M. Hastings, W. Kunnmann and E. Banks: Acta cryst. **21** (1966) Suppl. A. 95.
9) H. Forestier and G. Guiot-Guillain: CR Acad. Sci. **230** (1950) 1844; R. C. Sherwood, J. P. Remeika and H. J. Williams: J. appl. Phys. **30** (1959) 217; R. M. Bozorth V. Kramer and J. P.

Remeika: Phys. Rev. Letters **1** (1958) 3; H. Watanabe: J. Phys. Soc. Japan **14** (1959) 511.

10) I. E. Dzyaloshinskii: Soviet Physics -JETP **5** (1957) 1259; T. Moriya: Phys. Rev. **120** (1960) 91.

11) F. Wittmann und F. Pobell: Z. Naturforsch. **21a** (1966) 831.

12) F. Wittmann: Phys. Letters **24A** (1967) 252.

13) A. Hudson and H. J. Whitfield: J. Chem. Soc. (A) (1967) 376.

14) G. K. Wertheim: Phys. Rev. **121** (1961) 63; *Mössbauer Effect* (Academic Press, N. Y., 1964)

15) S. S. Hafner, B. J. Evans and G. M. Kalvius: Solid State Commun. **5** (1967) 17.

16) D. N. E. Buchanan and G. K. Wertheim: Bull. Amer. Phys. Soc. **7** (1962) 227.

17) Z. Friedman, H. Shaked and S. Shtrikman: Phys. Letters **25A** (1967) 9.