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Mössbauer and Magnetic Studies of Dicalcium ferrite ($Ca_2Fe_2O_5$)*

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In the antiferromagnetic compound $Ca_2Fe_2O_5$, the ferric ions occupy two non-equivalent sites. By means of Mössbauer studies in the temperature range 80 to 800° K, the variation of the magnetic hyperfine fields at both sites, as a function of temperature, is determined. It is found that all ferric ions order antiferromagnetically at a single Néel temperature, $T_N = (725 \pm 2)$ ° K.

From previous studies, the magnetic point group of this compound is known, and leads one to anticipate the existence of a ferromagnetic component in the ordered state. Magnetic measurements do, in fact, indicate the existence of such a component.

The experimental values obtained for the quadrupole splittings at both ferric sites are compared with point charge calculations. This leads to a complete disagreement, both in the ordered region and in the paramagnetic region, showing the inadequacy of the point charge model for the present case.

All the results are compared with the results of previous investigations on the same compound.

1. Introduction

In this paper we wish to report the results of a study initiated in our laboratory some years ago on dicalcium ferrite ($Ca_2Fe_2O_5$). During the last two years, quite a number of investigations on this and related compounds have been reported [1-12] with various disagreements between the results obtained by different investigators. We therefore wish to supplement these with our own results, and we shall try to clear the various questions on which contradictory results have been reported.

The crystallographic structure of $Ca_2Fe_2O_5$ has been investigated by Bertaut *et al* [13]. The unit cell is orthorhombic, belonging to the space group *Pcmn* (D_{2h}^{16}), with lattice constants: $a = 5.64$ Å, $b = 14.68$ Å, $c = 5.39$ Å. The Fe^{3+} ions occupy two non-equivalent sites with equal concentrations. One site is of nearly regular octahedral symmetry, while the other site is of nearly regular tetrahedral symmetry. The slight deviations from the ideal symmetry are clearly manifested through the appearance of a quadrupole splitting in the Mössbauer spectrum (see section 2).

The first reported Mössbauer studies on dicalcium ferrite were those by Pobell and Wittmann [1-3]. At room temperature, the Mössbauer spectrum is split into eleven well-resolved absorption lines, which reveals the existence of magnetic ordering. The values of the hyperfine fields on the Fe nuclei are rather large (see also section 2), which is typical for ferric ions. There exists a non-vanishing quadrupole interaction, which is small compared to the magnetic hyperfine interaction at all temperatures except those very close to the transition temperature. One would therefore expect, in principle, twelve absorption lines in the spectrum (six for each ferric site). An accidental overlap of two

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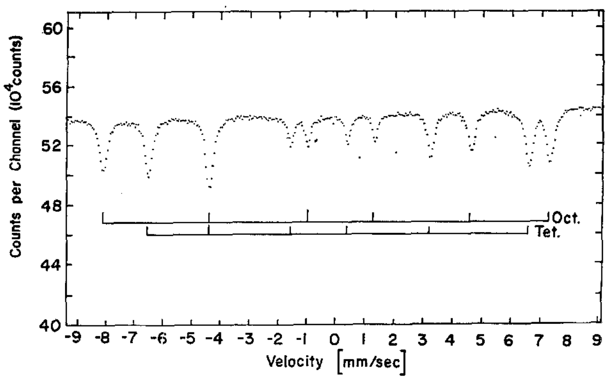

Figure 1 An unretouched spectrum of $Ca_2Fe_2O_5$ at room temperature. The absorption peaks due to the octahedral (oct) and the tetrahedral (tet) ferric sites are indicated.

lines, however, reduces this number to eleven. The identification of the lines which belong to the nuclei in the tetrahedral and octahedral sites has been accomplished by Pobell and Wittmann [1] by partial substitution of Fe^{3+} ions by diamagnetic Al^{3+} ions, which are known to go preferentially into the tetrahedral site [14]. The Néel temperature which Pobell and Wittmann reported [3], (615 ± 4)° K, was found to be too low by about 110° K: Grant *et al* [7] reported: $T_N = (730 \pm 2)$ ° K, which is very close to the value we find (see section 2).

Geller *et al* [4] investigated the nature of the magnetic interaction in $Ca_2Fe_2O_5$ by preferential substitution of diamagnetic (Sc^{3+} or Ga^{3+}) ions for Fe^{3+} ions. These substitutions did not produce ferrimagnetism, which showed that the octahedral and tetrahedral sub-lattices must each be antiferromagnetic (*intra*-sub-lattice antiferromagnetism). It was further concluded by Geller *et al* [4] that the *inter*-sub-lattice interaction should most probably be antiferromagnetic too. These investigators suggested that the magnetic unit cell is identical to the chemical one.

The next step was obviously the actual determination of the exact magnetic structure. This was accomplished independently by a Mössbauer study, utilising polarised γ-radiation on a single crystal of $Ca_2Fe_2O_5$ [5] and by neutron diffraction studies [10, 11]. All these experiments indicate that the direction of the sub-lattice magnetisation is parallel to the c-axis. The diffraction data confirm the previous assumptions of Geller *et al* [4] concerning the magnetic structure. The magnetic space group as determined from the neutron diffraction experiments [11] is *Pcm'n'*, from which the magnetic point group *mm'm'* follows. This in turn permits a ferromagnetic component along the *a*-axis. In measurements of the magnetisation as a function of temperature, a spontaneous magnetic moment was found to exist below the Néel temperature (see section 2).

2. Experimental and Results

$Ca_2Fe_2O_5$ was obtained by mixing stoichiometric ratios of $CaCO_3$ and Fe_2O_3. The mixture was ground to fine powder, pressed into pellets and heated to 1350° C in an oxygen atmosphere for 6 h. The product was checked by X-ray powder photographs. No extra lines were found, except for those consistent with the known space group of $Ca_2Fe_2O_5$ ($D_{2h}{}^{16}$).

Mössbauer spectra were taken on a constant velocity, automatic recording spectrometer* in the temperature range from 80 to 800° K. The absorber was contained in a variable temperature furnace (for high T measurements) or a cryostat (for low T measurements)†. The source, which was kept at room temperature, was Co^{57} in Pd‡. An unretouched spectrum, obtained at room temperature, is shown in fig. 1. As is clearly seen from the spectrum, the hyperfine (hf) field at the octahedral site is significantly larger than at the tetrahedral site. It should be further noted that the quadrupole splitting at the octahedral site is negative, whereas at the tetrahedral site it is positive.§ In fig. 2, we show a number of spectra

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*Manufactured by "Elron", Electronic Industries, Haifa, Israel.

†Furnace and cryostat manufactured by "Ricor", Cryogenic and Vacuum Systems of Israel, En-Harod Ihud, Israel.

‡Purchased from New England Nuclear Corporation, Boston, Mass, USA.

§The sign convention here is the usually accepted one, see e.g. G. K. Wertheirn, "Mössbauer Effect, Principles and Applications" (Academic Press, New York, 1964) Chap. VII.

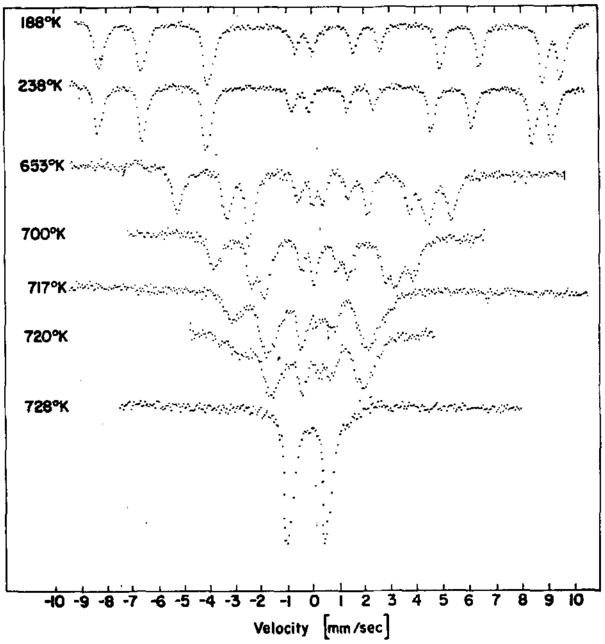

Figure 2 Some spectra of $Ca_2Fe_2O_5$ at various temperatures, from well below the Néel temperature (T_N), to a temperature above T_N.

obtained at various temperatures. These clearly show the collapse of the hf field as the Néel temperature is approached from below. From the analysis of the spectra we obtained the values of the hf field at both ferric sites, and these are plotted in fig. 3, against temperature. At 83° K we measured: H_n(oct) = (537 ± 5) KOe, H_n (tet) = (484 ± 5) ° K, in good agreement with results obtained elsewhere [6, 7].

The Néel temperature was determined in the following manner: The velocity was fixed at a value which corresponds to a paramagnetic peak (see fig. 2, spectrum at 728° K). The absorber was heated to 780° K, and then slowly cooled. The transmission rate was recorded as a function of temperature. The same procedure was repeated

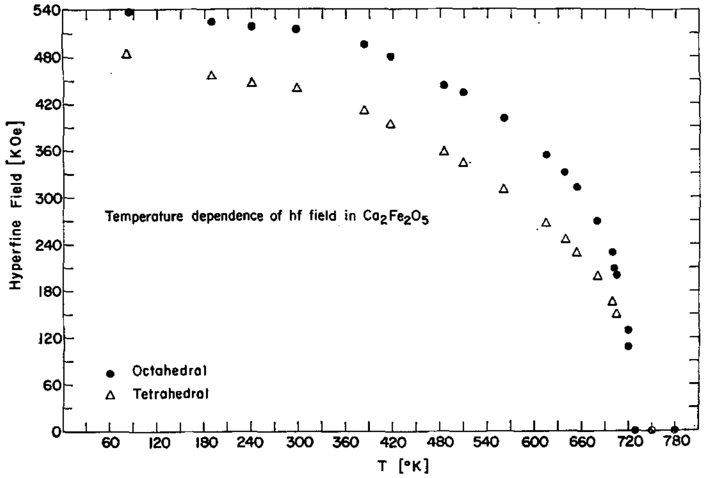

Figure 3 The experimental values of the hf field at the site of the Fe nucleus versus temperature, for the octahedral site (circles), and for the tetrahedral site (triangles).

in the opposite direction (i.e. heating from below T_N to above T_N). A sharp decrease in counting rate (while heating) or an increase (while cooling), determined the Néel temperature. In this manner we found: $T_N = (725 \pm 2)\ ^\circ$ K. The error in the determination comes from slight thermal hysteresis effects. The same method has been applied independently by Geller *et al* [9], who reported $T_N = (730 \pm 2)\ ^\circ$ K in a previous study [7]. At any rate, it was clearly established that $Ca_2Fe_2O_5$ has a single transition temperature, which is the ordering temperature of both the tetrahedral and the octahedral sub-lattices, and not two different transitions, as was suggested by Whitefield [6]. Furthermore, the determination of $T_N = 615^\circ$ K by Wittmann and Pobell [2-3] is too low by about 110°.

The quadrupole splitting (ΔE_Q) was measured from the spectra, both in the ordered and in the paramagnetic states. In the antiferromagnetic region, the quadrupolar interaction is small relative to the magnetic hf interaction at all temperatures except very close to T_N (where its determination is difficult anyway because of the overlap of various absorption lines). Hence, it can be regarded as a small perturbation to the magnetic hf interaction, and then we have*

$$\Delta E_Q{}^{(M)} = \frac{1}{2}\, eQV_{\mathrm{HH}} \qquad (1)$$

where the superscript M refers to the magnetic state, Q is the quadrupole moment of the $I = 3/2$ nuclear level of Fe^{57}, and V_{HH} is the component of the electric field gradient (EFG) tensor at the site of the nucleus, taken along the direction of the sub-lattice magnetisation. We find that the variation with temperature of $\Delta E_Q{}^{(M)}$ is negligible as in fact can be expected for Fe^{3+} compounds (see section 3). We measured in the range 80 to 680° K:

$$\Delta E_Q{}^{(M)}\,(\mathrm{oct}) = (-\,0.54 \pm 0.03)\ \mathrm{mm/sec}$$
$$\Delta E_Q{}^{(M)}\,(\mathrm{tet}) = (+\,0.70 \pm 0.03)\ \mathrm{mm/sec}$$

Above T_N, the measurement of ΔE_Q yields the full value of the quadrupole splitting, namely:

$$T > T_N : \Delta E_Q = \frac{1}{2}\, eV_{zz}Q\left(1 + \frac{\eta^2}{3}\right)^{\frac{1}{2}} \qquad (2)$$

where

$$\eta = (V_{xx} - V_{yy})/V_{zz}$$

and V_{xx}, V_{yy}, V_{zz} are the diagonal components of the EFG tensor in its principal co-ordinate system. We measured:

$$\Delta E_Q = (1.38 \pm 0.03)\ \mathrm{mm/sec}$$

at various temperatures from above T_N to 800° K, for both tetrahedral and octahedral sites. This is somewhat surprising in view of the different crystallographic environments of the two types of Fe^{3+} ions.

In order to check the possibility of the appearance of a spontaneous magnetic moment below T_N, as inferred from the group theoretical argument (section 1), we performed measurements of spontaneous magnetisation versus temperature. The measurements were taken on a Foner type vibrating sample magnetometer [15]. The sample was cooled from above T_N in a magnetic field, down to room temperature, and the magnetic field was then turned off. The spontaneous moment was measured as a function of temperature while heating the sample through T_N and above. A spontaneous magnetic moment, which decreased with temperature and disappeared discontinuously at T_N was detected. The result is shown in fig. 4. The M versus T curve has a shape which is reminiscent of the $M(T)$ curve for barium ferrite ($BaFe_{12}O_{19}$) [16]. The

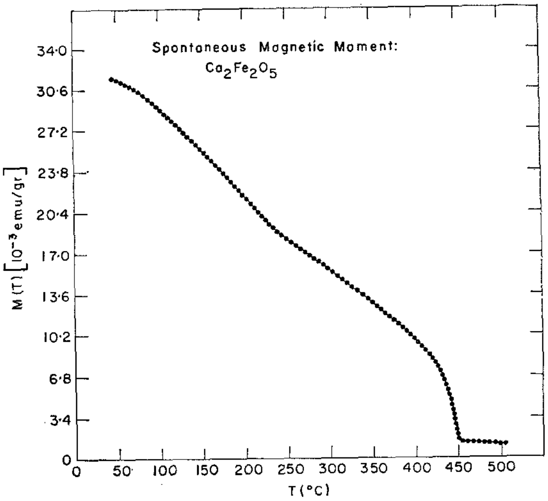

Figure 4 Spontaneous magnetic moment (M) as a function of temperature (T) in $Ca_2Fe_2O_5$. The sample was heated to above T_N, cooled in an external magnetic field to room temperature, and the field was then turned off. The curve shows $M(T)$ obtained while heating from 50 to 550° C.

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*The sign convention here is the usually accepted one, see e.g. G. K. Wertheirn, "Mössbauer Effect, Principles and Applications" (Academic Press, New York, 1964) Chap. VII.

Néel temperature of $Ca_2Fe_2O_5$ is very close to the Curie temperature of barium ferrite [17] ($T_c = 738°$ K). Even very small traces of Ba^{2+} in the starting materials from which our compound was made, can therefore also explain this behaviour. We cannot, at this stage, completely disregard the possibility, that in addition to $Ca_2Fe_2O_5$, small traces of some mixed barium-calcium ferrites were also present, such that their transition temperature was the same as T_N of the major product. We tend, however, to believe that the symmetry arguments which led us to expect a ferromagnetic component in the crystallographic a-direction lend support to our belief that such a component does in fact exist, and the spontaneous moment detected is due to $Ca_2Fe_2O_5$. Magnetic measurements on single crystals should resolve this question conclusively.

3. Discussion

3.1. Hyperfine Fields

The values obtained for the hf fields at the ferric nuclei are quite typical. The saturation value for H_n at the octahedral site ($\sim$ 550 KOe) is larger than at the tetrahedral site ($\sim$ 480 KOe), a situation often encountered in compounds where the ferric ions occupy similar sites (octahedral and tetrahedral)*. If one assumes that $H_n(T)$ is proportional to the sub-lattice magnetisation, $M(T)$, an assumption which is fairly justified for Fe^{3+} ions†, then this behaviour is directly correlated to the behaviour of the sub-lattice magnetisations at both sites. In this context it is worth mentioning, that an attempt to describe the temperature dependence of the reduced hf field $H_n(T)/H_n(0) = M(T)/M(0)$, versus T/T_N by a Brillouin function of $S = 5/2$, gives a much better fit for the octahedral site than for the tetrahedral site‡, although the fit is not too good in either case. It seems to us that Whitefield's [6] attempts to extrapolate the values of T_N for both ferric sites from such a fit are the source of the excessively high value he obtains for T_N at the octahedral site (760° K), and more seriously, for the assumption, which was found to be wrong, that there exist two transition temperatures.

3.2. Point Charge Calculation of the EFG's

In ferric compounds, the ionic ground term is ^6S. Hence, in the weak crystal field approximation, $L = 0$, and the direct contribution of the electrons of the ion to the EFG at the site of its nucleus vanishes. The major contribution to the EFG is therefore that of the surrounding ions. This contribution is amplified by the effect of the polarisation of the electronic shells of the ion itself, which is described by the Sternheimer antishielding factor $(1 - \gamma_\infty)$ [18].

For the calculation of the EFG by the customary point charge model, we represent each ion by an equivalent point charge situated at the ionic site, with a charge equal to ne, n being the valency ($n = +2$ for Ca^{2+}, $+3$ for Fe^{3+} and -2 for O^{2-}). We then calculate:

$$V_{ij}' = e\Sigma z_s r_s^{-5}[3(r_s)_i(r_s)_j - r_s^2\delta_{ij}] \qquad i,j = x, y, z \tag{3}$$

and the summation extends in principle over all ions in the lattice except for the ion in question. In practice we define a sphere around the Fe^{3+} ion, and include all ions within this sphere. In each step the radius of the sphere is increased, until convergence is obtained. The calculation was performed for an Fe^{3+} ion in a tetrahedral site and in an octahedral site separately. For each of the two calculations, about 400 000 ions were included in the final step. The result was multiplied by $(1 - \gamma_\infty)$, where we took $\gamma_\infty = -9.14$ [19], so we have:

$$V_{ij} = V_{ij}'(1 - \gamma_\infty) \tag{4}$$

For the evaluation of the quadrupole splitting, one needs the value of Q, the quadrupole moment of the $I = 3/2$ nuclear level of Fe^{57}. For this quantity, there is quite a spread of the values reported in the literature, ranging from 0.1 barn [20] to 0.41 barn [21]. We chose the value of $Q = 0.30$ barn, which has been deduced recently [22]. In units relevant to Mössbauer experiments, we obtain for the EFG tensor:

In the octahedral site:

$$\frac{1}{2}eQV_{ij}\,(\text{mm/sec}) = \begin{array}{c} \begin{array}{ccc} x & y & z \end{array} \\ \begin{bmatrix} -0.56 & 0.26 & 0.0045 \\ 0.26 & 0.26 & 0.10 \\ 0.0045 & 0.10 & 0.30 \end{bmatrix} \end{array} \tag{5}$$

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*Similar behaviour was found in garnets and other cases (see [16]).

†Fe^{3+} has the electronic configuration $[Ar]3d^5$, which leads to the ground term $^6S_{5/2}$, with $L = 0$. Hence in a weak crystal field (high spin states), there is no orbital or dipolar contribution to H_n, which is therefore proportional to $<S>$ and hence to the sub-lattice magnetisation

‡In fact the same conclusion can be reached from fig. 4 of Whitefield's paper (see [6]).

In the tetrahedral site:

$$\frac{1}{2}\,eQV_{ij}\,(\text{mm/sec}) = \begin{array}{c} \begin{array}{ccc} x & y & z \end{array} \\ \begin{bmatrix} 0.95 & 0 & 0.36 \\ 0 & -1.49 & 0 \\ 0.36 & 0 & 0.54 \end{bmatrix} \end{array} \quad (6)$$

where the x, y, z axes are chosen parallel to the crystallographic a, b, c-axes, respectively. In the antiferromagnetic state, remembering that the direction of the sub-lattice magnetisation is parallel to the c-axis, we therefore have:

$$\Delta E_Q{}^{(M)}\ (\text{calculated, oct}) = +\ 0.30\ (\text{mm/sec})$$

versus:

$$\Delta E_Q{}^{(M)}\ (\text{experimental, oct}) = -\ 0.54\ (\text{mm/sec})$$

and

$$\Delta E_Q{}^{(M)}\ (\text{calculated, tet}) = +\ 0.54\ (\text{mm/sec})$$

versus:

$$\Delta E_Q{}^{(M)}\ (\text{experimental, tet}) = +\ 0.70\ (\text{mm/sec})$$

The disagreement cannot be attributed to a wrong value of Q, because of the disagreement in the signs.

In the paramagnetic state, the situation is no better. From the calculated EFG tensor, one can easily calculate the expected splitting in the paramagnetic state*, obtaining

$$\Delta E_Q\ (\text{calculated, tet}) = 1.57\ (\text{mm/sec})$$
$$\Delta E_Q\ (\text{calculated, oct}) = 0.65\ (\text{mm/sec})$$

whereas the experimental value is: 1.38 (mm/sec) at *both* sites.The complete disagreement suggests, in our opinion, that the point charge model is far too crude an approximation, and does not describe the physical situation properly. We might add here, that dipolar contributions from the oxygen ions have been neglected in our calculation. Artman [21] took such contribution into account in his point charge calculations for αFe_2O_3, and found that they amount to about 20% of the calculated value in that case. The discrepancy in the case of $Ca_2Fe_2O_5$ is so drastic, that such a correction cannot probably change the situation. Wittman [8] has also reported the results of point charge calculations on $Ca_2Fe_2O_5$ and Ca_2FeAlO_5. The values he obtains for both compounds are very close. The curious fact about these results is that the fit for Ca_2FeAlO_5 is much better than for $Ca_2Fe_2O_5$. In that compound, the magnetic axis is parallel to the crystallographic a-direction, and hence the signs of $\Delta E_Q{}^{(M)}$ (calculated) agree with experiment. Furthermore, in Ca_2FeAlO_5 in the paramagnetic region, Wittman [8] reports two resolved doublets, one for each ferric site. However, Ca_2FeAlO_5, although apparently very close in structure to $Ca_2Fe_2O_5$ [13], has been found to belong to a *different* space group [23], namely: *Icmm*, and its magnetic structure differs appreciably from that of $Ca_2Fe_2O_5$ [12]. The apparent fit obtained for Ca_2FeAlO_5 is therefore, in our opinion, rather accidental, and should not be considered as a proof for the validity of the model, as the misfit in the case of $Ca_2Fe_2O_5$ shows.

3.3. Magnetic Structure

As already mentioned, the data obtained from neutron diffraction experiments [10-11] indicate that the magnetic space group of $Ca_2Fe_2O_5$ below T_N is *Pcm'n'*, from which the magnetic point group *mm'm'* follows. The interesting point to be checked, in this connection, was the possible existence of a weak ferromagnetic component in the a-direction. Our experimental results (section 2) do, in fact, indicate the existence of a spontaneous macroscopic magnetic moment below T_N, but we have indicated the possible doubts one can still have in this connection. Magnetic measurements on single crystals should resolve this question conclusively.

After completing this study, we learned that Takeda *et al* [24] have also performed magnetic measurements and neutron diffraction studies on $Ca_2Fe_2O_5$. Their results agree with earlier studies [10-11]. They report: $T = 720°$ K. Of particular interest is the fact that they also find a weak ferromagnetic component which has a very similar T-dependence to what we find. Takeda *et al* [24] explain this fact as due to the Dzyaloshinski-Moriya interaction, an interpretation which leads to the same conclusion as our symmetry arguments.

The experimental fact of the existence of this moment, however, needs in our opinion a final confirmation by measurements on single crystals.

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