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Mössbauer Effect Study of FeOCl

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A Mössbauer effect study has been made of FeOCl over the temperature range 1.96–298°K. At 298°K the isomer shift and quadrupole splitting (ΔE_Q) are +0.623(4) and 0.914(4) mm/sec, respectively, typical of a trivalent iron ion in an asymmetric environment. Magnetic ordering is observed below 68°K; the relevant parameters at 1.96°K being: isomer shift, +0.768(4) mm/sec; ΔE_Q, 1.083(4) mm/sec; $\frac{1}{2}e^2qQ$, 0.339(4) mm/sec; $|\eta'|$, 0.36; H_{eff}. 438(4) kOe. The principle axis of the electric field gradient tensor is shown to be at 90° to the direction of H_{eff} and the component of the electric field gradient in the direction of H_{eff} is positive. A comparison is made with the published parameters for γ-FeOOH, which has a similar structure.

Ferric oxychloride, FeOCl, crystallizes in a layer-type structure similar to that of the mineral lepidocrocite, γ-FeOOH (*1*), which is characterized by double-layered sheets of oxygen octahedra linked together by shared edges, each filled with a ferric ion (*2*). Each octahedron has four oxygen atoms and two hydroxyl oxygens at its vertices, the bridging being through the nonhydroxyl oxygens. FeOCl has the same double sheet of linked octahedra but with the chloride ions on the outsides of adjacent layers forming a close-packed array.

Mössbauer effect measurements have shown γ-FeOOH to be an antiferromagnet with a Néel temperature (T_N) of 73°K and a magnetic hyperfine field acting on the iron nucleus (H_{eff}) of 460 ± 5 kOe (*3*). Although Mossbauer effect studies have been made on FeOF, showing it to be antiferromagnetic ($T_N = 315$°K, $H_{\mathrm{eff}} = 485 \pm 10$ kOe), it has the rutile structure, not at all related to FeOCl. This article reports Mössbauer effect measurements for FeOCl taken over the temperature range 1.96–298°K.

Experimental

FeOCl was prepared by heating anhydrous ferric chloride (purified, sublimed—Fisher Scientific Company) in a stream of water-saturated oxygen at 200°C for 6 hr. X-ray powder diffraction of the product agreed with that recorded on ASTM Data Card 1-81. Chemical analysis agreed with the stoichiometry FeOCl.

The ^{57}Fe Mössbauer effect was measured with a Model NS-1 Mössbauer Spectrometer (Nuclear Science and Engineering Corporation, Pittsburgh, Pennsylvania) operating in the constant acceleration mode. The 14.4-keV γ-radiation from a source of ^{57}Co diffused into palladium (10 mCi) was detected with a gas proportional counter and collected with a 400-channel analyzer operating in time-sequence scaling mode. The source and drive were calibrated against a single crystal of sodium nitroprusside (National Bureau of Standards, Standard Reference Material No. 725). The quadrupole splitting for sodium nitroprusside was taken as 1.7048 ± 0.0025 mm/sec (*5*). Isomer shifts are reported with respect to the zero position of this standard. The data were reduced by a computer program which performed a nonlinear least-squares fit to the product of a series of absorption peaks having Lorentzian shapes on a parabolic base line, a result of our particular drive geometry. All of the variables (peak position, peak height, and peak half-width) were allowed to vary independently.

Cryogenic measurements were made in a variable-temperature Dewar (Andonian Associates, Incorporated, Waltham, Massachusetts) with the source at room temperature. Temperature control was within ±0.5°K at liquid nitrogen temperatures and ±0.01° at liquid helium temperatures. The powdered sample was mounted between two beryllium disks (0.010 mm thick) which were then mounted on a copper mounting in which both a

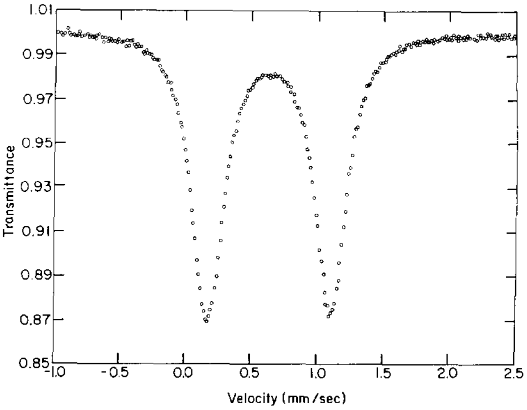

FIG. 1. Mössbauer spectrum of FeOCl at room temperature. Velocity scale is relative to sodium nitroprusside.

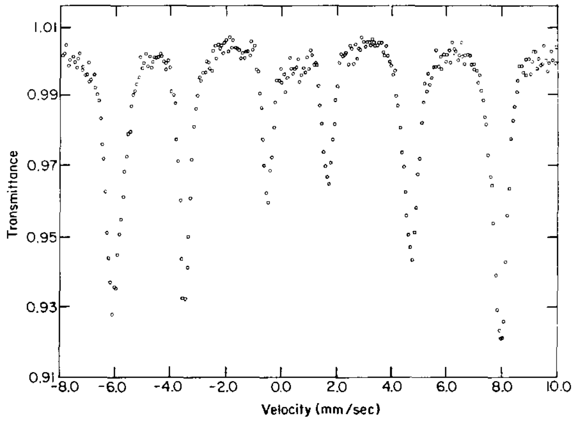

FIG. 2. Mössbauer spectrum of FeOCl at 1.96°K. Velocity scale is relative to sodium nitroprusside.

copper-constantan thermocouple and a carbon resistor were embedded for temperature measurement and control. The sample contained 20 mg/cm^2 of FeOCl.

Results and Discussion

Figure 1 illustrates the room temperature (298°K) Mössbauer resonance spectrum of FeOCl, with measured values of +0.623(4) mm/sec for the isomer shift and 0.914(4) mm/sec for the quadrupole splitting (ΔE_Q), values which are typical of high-spin trivalent iron in an asymmetric environment (*6*). Table I summarizes the Mössbauer parameters at 298° and 77°K. In lowering the temperature to 77°K, there is a moderate increase in isomer shift which can be accounted for by the second-order Doppler effect and a small increase in the quadrupole splitting.

It is instructive at this point to compare these values for FeOCl with those for γ-FeOOH (*7*). At 298°K, γ-FeOOH exhibits an isomer shift of $+0.65 \pm 0.06$ mm/sec (the value taken from Ref. (*7*), corrected relative to sodium nitroprusside by the addition of 0.17 mm/sec) and a quadrupole splitting of 0.54 ± 0.06 mm/sec; at 77°K the values are $+0.79 \pm 0.06$ mm/sec and 0.62 ± 0.06 mm/sec, respectively. The smaller values for the isomer shifts in FeOCl undoubtedly is the result of a slight increase in *s*-electron density at the iron nucleus relative to γ-FeOOH due to the slightly smaller electronegativity of chlorine. Most probably the quadrupole splittings are larger in FeOCl due to the increased distortion of the coordination polyhedron about the iron site since the chlorine ion is substantially larger than the oxygen ion.

TABLE I[a]

	298°K	77°K
Isomer shift[b]	+0.623	+0.729
ΔE_Q	0.914	0.920

[a] All velocities in mm/sec with an estimated error of 0.004 mm/sec.

[b] Relative to sodium nitroprusside.

At 1.96°K, the six-line spectrum characteristic of an iron nucleus in a magnetically ordered material is observed (Fig. 2). Using the formulation of Johnson (*8*) this spectrum can be analyzed to give the parameters listed in Table II, where g_0 and g_1 are the splittings of the nuclear ground and excited levels, respectively; ΔE_Q is the quadrupole splitting equal to $\frac{1}{2}e^2qQ(1+\eta^2/3)^{1/2}$; η is the asymmetry parameter, equal to $(V_{xx}-V_{yy})/V_{zz}$) which defines

TABLE II

MÖSSBAUER PARAMETERS OF FeOCl AT 1.96°K

g_0 (mm/sec)	5.18
g_0/g_1	1.78
Isomer shift (mm/sec)[a, b]	+0.768
ΔE_Q (mm/sec)[b]	1.083
$\frac{1}{2}e^2qQ$ (mm/sec)[b]	0.339
η	5.25
H_{eff} (kOe)	438(4)
$\frac{1}{2}e^2q'Q$ (mm/sec)[b]	−1.060
$\lvert\eta'\rvert$	0.36

[a] Relative to sodium nitroprusside.

[b] Estimated error of 0.006 mm/sec.

the shape of the electric field gradient; and H_{eff} is the effective magnetic field acting on the iron nucleus, calculated from g_0 using a value of 0.09024 nuclear magnetons for the magnetic moment of the iron nucleus (*9*).

This analysis is predicated on the assumption that the major axis of the electric field gradient tensor is either parallel or perpendicular to the direction of H_{eff} (*10*). In the case of FeOCl this seems to be a good approximation since the values for H_{eff} calculated from the measured ground and excited state splittings are the same within experimental error, a necessary consequence of the colinearity of the two directions. The value of g_0/g_1 is in reasonable agreement with the established value of 1.75 (*9*). Furthermore, the component of the electric field gradient tensor in the direction of H_{eff} is positive, since the $I_z = \pm\frac{3}{2}$ levels are raised[1] (the separation of lines 5 and 6 is greater than that of lines 1 and 2, numbering from left to right). The fact that $\eta > 1$ indicates that the major axis of the electric field gradient tensor is perpendicular to H_{eff} and, following the usual convention, transforming coordinates so that $0 \leqslant |\eta| \leqslant 1$ we arrive at new values for $|\eta'|$ and $\frac{1}{2}e^2q'Q$ of 0.36 and −1.060 mm/sec, respectively, the prime indicating the new coordinate system.

From a plot of H_{eff} versus T it is estimated that the magnetic ordering temperature is 68 ± 2°K. It should be emphasized that this is a visual estimation since above 55°K the resonance peaks broaden to such an extent that the exact measurement of the effective hyperfine field becomes difficult, and, in addition, the H_{eff} versus T curve does not follow a Brillouin function.

γ-FeOOH has values (*3*) of 460 ± 5 kOe and 73°K for H_{eff} and T_{N}, respectively; in each case slightly higher than the values for FeOCl [438(4) kOe and 68 ± 2°K]. In all probability this reflects the weaker bonding between layers in FeOCl due to the absence of the hydrogen bonding present in γ-FeOOH. A similar effect is shown in the difference between the γ form of FeOOH and the α and β forms (*3*).

In summary, we have reported the Mössbauer parameters of FeOCl at 1.96, 77, and 298°K. The temperature dependence of H_{eff} indicates a magnetic ordering temperature of 68 ± 2°K. At 1.96°K, the major axis of the electric field gradient tensor is at 90° to H_{eff}. The electric field gradient has an asymmetry parameter of 0.36.

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References

1. A. F. Wells, "Structural Inorganic Chemistry," 3rd ed., Oxford Univ. Press, London, 1962.
2. F. J. Ewing, *J. Chem. Phys.* **3**, 203 (1935).
3. C. E. Johnson, *Proc. Phys. Soc. London Solid State Phys.* **2**, 1996 (1969).
4. J. Chappert and J. Portier, *Solid State Commun.* **4**, 185 (1966).
5. R. W. Grant, R. M. Housley, and U. Gonser, *Phys. Rev.* **178**, 523 (1969).
6. G. K. Wertheim, "Mössbauer Effect: Principles and Applications," Academic Press, New York, 1964.
7. M. J. Rossiter and A. E. M. Hodgson, *J. Inorg. Nucl. Chem.* **27**, 63 (1965).
8. C. E. Johnson, *Proc. Phys. Soc. London* **88**, 943 (1966).
9. P. R. Locher and S. Geschwind, *Phys. Rev.* **A139**, 991 (1965).
10. S. Chandra, PhD Thesis, Boston University, 1967, unpublished.

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[1] Using the usual sign conventions; see, for example, Ref. (*7*).