[9]M. Lax, Phys. Rev. 145, 110 (1966).
[10]I. R. Senitzky, Phys. Rev. 137, A1635 (1965).
[11]W. H. Louisell and L. R. Walker, Phys. Rev. 137, B204 (1965).
[12]R. H. Dicke, Phys. Rev. 93, 99 (1954).
[13]V. F. Sears, Proc. Phys. Soc. (London) 84, 951 (1964).
[14]R. M. Sillitto, *Non-Relativistic Quantum Mechanics* (Quadrangle Books, Chicago, 1960).
[15]I. Waller, R. de L. Kronig, and J. H. Van Vleck, in *Spin-Lattice Relaxation in Ionic Solids*, edited by A. A. Manenkov and R. Orbach (Harper and Row, New York, 1966).
[16]N. W. Dalton and D. W. Wood, Solid State Commun. 7, 1271 (1969).
[17]R. J. Elliott and J. B. Parkinson, Proc. Phys. Soc. (London) 92, 1024 (1967).
[18]E. R. Muller and J. W. Tucker, Proc. Phys. Soc. (London) 88, 693 (1966).
[19]K. W. H. Stevens and H. A. M. Van Eekelen, Proc. Phys. Soc. (London) 92, 680 (1967).
[20]D. L. Mills, Phys. Rev. 139, A1640 (1965).
[21]P. L. Scott and C. D. Jeffries, Phys. Rev. 127, 32 (1962).
[22]C. E. Johnson and H. Meyer, Proc. Roy. Soc. (London) A253, 199 (1959).
[23]J. Rae, Bull. Classe Sci. Acad. Roy. Belg. 55, 1040 (1969).

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"Overlap" Contributions to the Electric-Field-Gradient Components at the Fe^{3+} Site in FeOCl

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Using the simple Sawatzky model, we have made an evaluation of the "overlap" contributions to the electric-field-gradient (EFG) components at the non-axially-symmetric Fe^{3+} site in FeOCl. The modifications to the EFG components calculated previously by lattice-sum methods are considerable. For O^{2-} and Cl^- polarizibility α values of 1.0 Å^3, it was possible both to match the experimental asymmetry parameter η value of 0.32 and to get a $Q(Fe^{57m})$ value of 0.19 b, close to the ferrous consensus.

Recently there appeared a determination of the Fe^{57m} nuclear-quadrupole coupling parameters pertinent to the non-axially-symmetric Fe^{3+} site in FeOCl.[1] Unfortunately, the fit of a self-consistent monopole–point-dipole lattice-sum electric-field-gradient (EFG) calculation to these data was not very satisfactory. The dipole contributions to the EFG, for O^{2-} and Cl^- polarizibilities α varying over the range 1–3 Å^3, were at times comparable to the monopole sums (cation polarizibility was neglected). The only way that the EFG asymmetry parameter η could be properly fitted within the α range used was to set $\alpha_O = \alpha_{Cl} = 1$. However, this led to a calculated $Q(Fe^{57m})$ of 0.33 b, which, in the light of recent analyses,[2] is probably much too large. We present in this paper an evaluation, in this system, of the EFG contributions due to the overlap distortion of the Fe^{3+} closed-shell orbitals by the ligands. Such calculations have recently been made in α-Al_2O_3 and α-Fe_2O_3 by Sawatzky and associates[3] and by Sharma.[4] From their analyses in sapphire-type geometries, these authors have obtained values for $Q(Al^{27})$ and $Q(Fe^{57m})$ which agree very well with other data. We use the more simple Sawatzky formulation here.

Clearly, the non-axially-symmetric Fe^{3+} site in FeOCl provides a more searching test of theoretical EFG calculations than the symmetric Fe^{3+} site in α-Fe_2O_3. Also, unlike α-Fe_2O_3, the lattice-sum calculations in FeOCl are relatively insensitive to variations in crystallographic parameters.[1] However, as noted above, anion polarizibility enters relatively prominently here. Before proceeding further, we summarize the FeOCl Mössbauer-effect results. The quadrupole splitting ΔE_Q was found to be 0.916 ± 0.001 mm/sec; the η value was 0.32 ± 0.03; and the x, y, z principal axes of the EFG were parallel to the crystallographic c, b, a axes, respectively ($c < a < b$) with V_{zz} negative.

In this system, Fe^{3+} is octahedrally coordinated, having as nearest neighbors two oxygen ions at 1.964 Å, another two oxygens at 2.100 Å, and two chlorines at 2.368 Å. In calculating the overlap integrals, we have noted the arguments of Sawatzky and associates in assessing the relative magnitudes of various contributions to the overlap. Therefore, we consider here the overlap of the Fe^{3+} $2p$ and $3p$ orbitals with (i) the oxygen $2p$ orbitals and (ii) the chlorine $3p$ orbitals. The basic equation for the EFG contribution $(V'_{zz})_k$ from each *set k* of 2

TABLE I. Overlap integrals and geometrical parameters for the $(FeO_4Cl_2)^{5-}$ complex in FeOCl.[a]

Fe ligand distance (Å)	S^{σ}_{3p}	S^{π}_{3p}	S^{s}_{3p}	S^{σ}_{2p}	S^{π}_{2p}	S^{s}_{2p}	$\cos\theta$	$\sin\theta$	$\cos\phi$	$\sin\phi$
$(Fe-O)_1$ = 1.964	7.8230	2.6524	3.5892	0.45626	0.14600	0.16399	−0.2716	0.9624	0	±1.0
$(Fe-O)_2$ = 2.100	6.3887	2.0101	2.5414	0.36342	0.10940	0.11364	−0.6182	0.7860	±1.0	0
(Fe—Cl) = 2.368	5.3002	1.5560	2.2949	0.29248	0.08049	0.10060	0.7168	0.6973	±1.0	0

[a]The S values listed are to be multiplied by 10^{-2}.

ligands is [see Eq. (4), Ref. 3(b)]

$$(V'_{zz})_k = -\tfrac{8}{5}e\,(3\cos^2\theta_k - 1)\,[\,(S^k_{3p})^2\langle 1/r^3\rangle_{3p} + (S^k_{2p})^2\langle 1/r^3\rangle_{2p} + 2S^k_{2p}\,S^k_{3p}\,\langle 1/r^3\rangle_{2p,3p}\,]\,, \qquad (1)$$

where the $2p$ and $3p$ designations refer to the Fe^{3+} wave functions. The single-electron overlap coefficients S^k_{np} are compounded as follows:

$$S^k_{np}\,S^k_{mp} = S^{\sigma k}_{np}S^{\sigma k}_{mp} - S^{\pi k}_{np}S^{\pi k}_{mp} + S^{sk}_{np}S^{sk}_{mp}\;.$$

The V'_{xx} and V'_{yy} contributions follow from Eq. (1) merely by replacing the $3\cos^2\theta_k - 1$ term with $3\sin^2\theta_k\cos^2\phi_k - 1$ and $3\sin^2\theta_k\sin^2\phi_k - 1$, respectively. These angles (θ_k, φ_k) specify in the usual way the angular orientation of the ligands with respect to our coordinate system. The $3p$ wave function for Cl^- was obtained using the Herman-Skillman computer routine[5]; the O^{2-} and Fe^{3+} wave functions were obtained from Watson's paper[6] and report,[7] respectively. The values of $\langle r^{-3}\rangle$ for the Fe $3p$, Fe $2p$, and Fe $3p$, $2p$ wave function combinations were 56.17, 461.96, and − 153.13 a.u., respectively. The S-type overlap integrals were evaluated by the methods of Mulliken[8] and his associates. Additional overlap calculations were made by one of us (G. A. S.) using wave functions from various sources. The numerics entering in Eq. (1) are listed in Table I.

The composite EFG then follows as

$$V_{ii} = (1 - R)\,(V'_{ii})_{\rm overlap} + (1 - \gamma_\infty)\,(V'_{ii})_{\rm lattice\ sum}\;. \qquad (2)$$

We take the R and γ_∞ shielding factors as 0.32[9] and − 9.14,[10] respectively. In Table II we list, for several different O^{2-} and Cl^- α values, the dipole moment values and the V_{ii} sums. For each combination of α's we list the V_{ii} sums with (below) and without (above) the overlap contributions. For each case, we have computed η; using this η and the calculated V_{zz} value, we have computed $Q(Fe^{57m})$ from the experimental ΔE_Q result. A negative value of η in Table II indicates that the calculated x and y EFG axes are interchanged from the experimental ordering.

The apparently good Q fit of the zero-α lattice-sum data is untenable because of the reversal of axes reflected in the sign of η. The lattice-sum data for the case $\alpha_O = \alpha_{Cl} = 1$ Å^3, as mentioned earlier, give an "exact" fit to η, and a Q of 0.33 b. Inclusion of overlap contributions seems to depress the calculated Q and η values for most of the entries in Table II. In the case $\alpha_O = \alpha_{Cl} = 1$ Å^3, we find an η of 0.31 and a Q of 0.19 b. This provides an excellent match for the experimental η value and for the current $Q(Fe^{57m})$ consensus.

We note that Sharma's overlap formulation[4] includes EFG contributions from the *ligand* valence orbitals. In his analysis, the nearest-neighbor

TABLE II. Evaluation of EFG components, η, and $Q(Fe^{57m})$.

α_O [a]	α_{Cl} [a]	p_O [b]	p_{Cl} [b]	V_{ii} [c]	η [d]	Q [e]
0	0	0	0	−3.07, 0.91, 2.16	−0.41	0.19
				−4.40, 1.78, 2.62	−0.19	0.14
1	1	0.159	0.361	−1.81, 1.19, 0.62	0.32	0.33
				−3.14, 2.06, 1.08	0.31	0.19
1.5	1	0.248	0.356	−1.31, 1.13, 0.18	0.73	0.43
				−2.64, 2.00, 0.64	0.52	0.22
2	1	0.346	0.350	−0.75, 1.06, −0.31	...	...
				−2.08, 1.93, 0.15	0.86	0.26

[a]The units used for α are Å^3.
[b]The units used for p are Å.
[c]The units used for V_{ii} are Å^{-3}. The V_{ii} are ordered as $i=a, b, c$. For each set of 2 values, the upper three V_{ii} represent the lattice-sum results. The lower three contain the overlap contributions as well.
[d]We define η as $(V_{cc}-V_{bb})/V_{aa}$.
[e]The units used for Q are b.

dipoles then would be subtracted from the lattice-sum dipole EFG computation. (The point charges on the nearest neighbors are corrected similarly.) This subtraction would remove almost all of the oxygen dipole contribution and reduce the chlorine dipole contribution considerably. It will be interesting to see what might ensue from a more sophisticated version of this model.

[1]R. W. Grant, H. Wiedersich, R. M. Housley, G. P. Espinosa, and J. O. Artman, Phys. Rev. B 3, 678 (1971).

[2]R. Ingalls, Phys. Rev. 188, 1045 (1969); J. Chappert, R. B. Frankel, A. Misetich, and N. A. Blum, Phys. Letters 28B, 406 (1969); Phys. Rev. 179, 578 (1969); H. R. Leider and D. N. Pipkorn, *ibid.* 165, 494 (1968); R. M. Housley and U. Gonser, *ibid.* 171, 480 (1968); A. J. Nozik and M. Kaplan, *ibid.* 159, 273 (1967); C. E. Johnson, Proc. Phys. Soc. (London) 92, 748 (1967); F. S. Ham, Phys. Rev. 160, 328 (1967); M. Weissbluth and J. E. Malling, J. Chem. Phys. 47, 4166 (1967). These are all ferrous data.

[3](a) G. A. Sawatzky and J. Hupkes, Phys. Rev. Letters 25, 100 (1970); (b) G. A. Sawatzky, F. van der Woude, and J. Hupkes, J. Phys. (Paris) (to be published).

[4]R. R. Sharma, Phys. Rev. Letters 25, 1622 (1970); 26, 563 (1971).

[5]These computations were made using a program furnished by the IBM Library.

[6]R. E. Watson, Phys. Rev. 111, 1108 (1958).

[7]R. E. Watson, MIT Solid State and Molecular Theory Group Report No. 12, 1959 (unpublished).

[8]R. S. Mulliken, C. A. Reike, D. Orloff, and H. Orloff, J. Chem. Phys. 17, 1248 (1949).

[9]R. Ingalls, Phys. Rev. 133, A787 (1964).

[10]R. M. Sternheimer, Phys. Rev. 130, 1423 (1963).