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Significance of the Lattice Contribution to Mössbauer Quadrupole Splitting: Re-Evaluation of the Fe^{57m} Nuclear Quadrupole Moment*

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We have considered in detail the lattice contribution to the electric-field gradient at the Fe^{57} nucleus in several ferrous compounds. Using x-ray crystallographic data and a high-speed computer, direct lattice-sum calculations have been carried out for $FeSiF_6\cdot 6H_2O$, $FeSO_4\cdot 7H_2O$, $FeCl_2\cdot 4H_2O$, and $FeCl_2\cdot 2H_2O$, yielding the magnitudes and signs of the lattice effect in these compounds. The results obtained ranged from negligible to substantial levels, in terms of the lattice contribution to the observed Mössbauer quadrupole splitting. Of particular importance is the inconsistency between our results and the analytic treatment given by Ingalls, which would predict a much larger lattice contribution with a sign opposite to that of the local electronic field gradient. On the other hand, we find that one cannot, in general, assume the effect of the lattice to be small, as has frequently been done. Using the computed lattice contribution to the electric-field gradient in $FeSiF_6\cdot 6H_2O$, and the experimentally measured low-temperature quadrupole splitting in this crystal, we have re-evaluated the nuclear quadrupole moment of the 14.4-keV state in Fe^{57} to be +0.20 b.

I. INTRODUCTION

THE significance of the direct lattice contribution to the electric-field gradient (EFG) at the Fe^{57} nucleus, and hence to the nuclear quadrupole hyperfine splitting (Q.S.) in ferrous compounds, is currently a subject of confusion in the literature. It is important that this question be resolved because the magnitude and sign of the lattice effect will influence not only the derived value of the Fe^{57m} nuclear quadrupole moment, but also the conclusions drawn concerning ligand symmetry, orbital splittings, and spin-orbit interaction in a variety of ferrous-containing crystals.

The total quadrupole splitting in ferrous compounds (Fe^{57}) is given by

$$\text{Q.S.}=\tfrac{1}{2}e^2qQ(1+\tfrac{1}{3}\eta^2)^{1/2}, \tag{1}$$

where Q is the nuclear quadrupole moment of the 14.4-keV state in Fe^{57} and the field gradient $q=V_{zz}/e$ and asymmetry parameter $\eta=(V_{xx}-V_{yy})/V_{zz}$ serve to specify the electric-field-gradient tensor in a principal axis system. We may express these latter quantities as

$$q=(1-R)q_{\text{val}}+(1-\gamma_\infty)q_{\text{lat}} \tag{2}$$

$$\eta q=(1-R)\eta_{\text{val}}q_{\text{val}}+(1-\gamma_\infty)\eta_{\text{lat}}q_{\text{lat}} \tag{3}$$

where q_{val}, η_{val} refer to the gradient produced by the charge distribution of the nonspherical $3d$ "valence" electron of the ferrous ion (^5D, $3d^6$) in a crystal field, and q_{lat}, η_{lat} arise from the charge distribution of all other ions in the lattice. The Sternheimer factors,[1,2] $(1-R)$ and $(1-\gamma_\infty)$, represent the effects of polarization of the ferric-like (^6S, $3d^5$) core by the EFG of the valence and lattice charge distributions.

It is generally agreed that the valence term accounts for the major part of the field gradient in ferrous compounds. The lattice contribution, however, has not been well studied, and will be of primary concern here. By definition we have

$$q_{\text{lat}}=\sum_i Z_i(3\cos^2\theta_i-1)/r_i^3, \tag{4}$$

where Z_i and (r_i, θ_i) are the charge and radial coordinates of the ith ion in the lattice, and the sum is over all ions in the lattice. A direct determination of q_{lat} by means of Eq. (4) requires an accurate knowledge of the positions and charges for all species in the crystal, and such information is currently available for relatively few compounds.

Ingalls[3] has estimated q_{lat} in terms of the ion orbital splitting parameters Δ_1 and Δ_2, which arise from crystal fields with lower than cubic symmetry. His treatment predicts that q_{lat} is always of opposite sign to q_{val}, and, with spin-orbit coupling, reduces the free-ion q by at least 17%. On the other hand, other authors[4–7] have assumed q_{lat} to be very small and have neglected it in the analysis and interpretation of Mössbauer Q.S. data.

II. THE LATTICE SUM CALCULATION

We have estimated q_{lat} for several ferrous compounds of well-determined crystal structure by using a point-charge model and performing the direct lattice summations on an IBM 7094/7040 computer. The compounds studied were ferrous fluosilicate hexahydrate,[8] ferrous sulfate heptahydrate,[9] ferrous chloride tetrahydrate,[10] and ferrous chloride dihydrate.[11] The calcu-

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TABLE I. Calculated results of the direct lattice contribution to the nuclear quadrupole hyperfine splitting in several ferrous compounds.

						First coordination sphere		
Compound	Q.S.$_{\text{lat}}$ (mm/sec)	$10^{-14}eq_{\text{lat}}$ (esu/cm^3)	η_{lat}	Q.S.$_{\text{exp}}$[a] (mm/sec)	Structure	Point symmetry	Q.S.$_{\text{fcs}}$ (mm/sec)	η_{fcs}
$FeSiF_6 \cdot 6H_2O$	-0.02 ± 0.01[b]	-0.027	0	-3.67	$Fe(H_2O)_6{}^{++}$	C_{3v}	$+0.03$	0
$FeSO_4 \cdot 7H_2O$								
site 1	$+0.08\pm0.02$	$+0.106$	0.82	±3.57[c]	$Fe(H_2O)_6{}^{++}$	C_i	-0.13	0.48
site 2	-0.08 ± 0.02	-0.111	0.59		$Fe(H_2O)_6{}^{++}$	C_i	···	···
$FeCl_2 \cdot 4H_2O$	-0.41 ± 0.10	-0.552	0.70	$+3.08$	$Fe(H_2O)_4Cl_2$	C_{2h}	-0.47	0.69
$FeCl_2 \cdot 2H_2O$	-0.10 ± 0.04	-0.130	0.31	$+2.63$	$Fe(H_2O)_2Cl_4{}^{=}$	weak[d] C_{2h}	$+0.26$	0.44

[a] The experimental data are all at 77°K, and are from the following sources: $FeSiF_6 \cdot 6H_2O$, (Refs. 19 and 22); $FeSO_4 \cdot 7H_2O$ (Refs. 20 and 22); $FeCl_2 \cdot 4H_2O$ (Refs. 20-22); $FeCl_2 \cdot 2H_2O$ (Ref. 4).

[b] The indicated uncertainty reflects the range of charge assignments (see text).

[c] The sign has not been experimentally determined.

[d] The symmetry is a slight distortion from D_{4h}.

lations were made by evaluating the 9-component EFG tensor

$$V_{ij}=\sum_k \frac{Z_k(3r_{ik}r_{jk}-\delta_{ij}r_k{}^2)}{r_k{}^5}, \qquad i,j=x,y,z \qquad (5)$$

in an arbitrary orthogonal coordinate frame, and then diagonalizing the tensor to generate the principal components V_{zz} and η. This procedure also yields the coordinates of the principal axes (PA) and is convenient for crystals of low symmetry where the PA are not obvious. The summation in Eq. (5) was carried out over the k ions of charge Z_k that are contained within a chosen radial distance from the central ferrous ion, and this radius of summation was systematically varied until convergence was attained. For the cases discussed here, a sphere of radius 25 Å was sufficient for convergence.

A primary restriction on the validity of carrying out the lattice summations using a point-charge model arises from the uncertainties in charge assignments. We have, in fact, performed the calculations over a range of charge assignments which are consistent with the character of the bonds involved. The assignments for the H_2O molecule were based on the results of a population analysis[12] of the SCF–LCAO wave functions for H_2O. It was assumed that the charge distribution in the free molecule is unchanged in the solid. The $SO_4{}^{=}$ ion charges were derived from Pauling's estimation[13] and the Si–F bond was taken as 70–90% ionic.[14,15] The charge distributions in the octahedral Fe^{++} complexes were obtained by assuming that the $Fe–OH_2$ bond is essentially ionic,[13,16,17] and the Fe–Cl bond is 60–80% ionic.[14–16] Experimental data on Mössbauer isomer shifts[16,17] are consistent with these assignments, but it should be noted that particularly in the case of the Fe–Cl bond, the higher degree of covalency renders the point-charge approximation less adequate, and a molecular orbital treatment is required for more accurate results.[18] However, the ranges of q_{lat} values obtained by varying the charge assignments were relatively narrow for the compounds studied here, and hence provide reasonable estimates for the present purpose. The results to be presented below correspond to the middle of the range. (We have not attempted to include induced multipole moments in our calculations because of the large uncertainties in ionic polarizabilities and the complexity they would add to the computations. For the cases considered here, their effects are expected to be quite small.)

III. RESULTS AND DISCUSSION

Our results are summarized in Table I, in terms of the quadrupole splitting produced by the lattice contribution to the electric-field gradient. The Q.S.$_{\text{lat}}$ was computed from q_{lat} using the revised value (see Sec. IV) of 0.20b for the nuclear quadrupole moment of the 14.4-keV state in Fe^{57}. In order to illustrate the significance of the lattice effect, we have listed the measured quadrupole splittings for each of the ferrous compounds.[4,19–22] The table also gives the symmetry of the first coordination sphere (fcs) around the ferrous ion, and the "lattice" contribution obtained when the summation is restricted to this immediate environment. It is immediately apparent that the importance of q_{lat} depends very strongly on the particular compound, being quite small for $FeSiF_6 \cdot 6H_2O$, somewhat greater

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for $FeSO_4\cdot 7H_2O$ and $FeCl_2\cdot 2H_2O$, and comprising a considerable fraction of the total $Q.S._{exp}$ for $FeCl_2\cdot 4H_2O$. Furthermore, the data in Table I show that consideration of only the nearest neighbors can lead to erroneous results which may differ from the converged summations not only in magnitude but also in sign.

Our results do not agree with the predictions of Ingalls.[3] For the case of $FeSiF_6\cdot 6H_2O$, the ground-state orbital wave function for the ferrous ion is known[19] and yields a negative value for q_{val}. Table I shows that the lattice contribution is also negative in this crystal, and hence not of opposite sign to q_{val}. On the other hand, the ferrous chloride hydrates both have q_{lat} of opposite sign to q_{val}, assuming that the reported assignments[3,4] of ground-state orbitals are correct. In addition, the magnitudes of q_{lat} for all the crystals are smaller than the minimum values predicted by Ingalls,[3] but certainly not all are negligible as assumed by others. The situation for $FeSO_4\cdot 7H_2O$ is complicated by the existence of two inequivalent Fe sites per unit cell. Out computed values of q_{lat} for the two sites have opposite sign, but the same magnitude (within the quoted uncertainty). It would be interesting to carry out sufficiently detailed experiments (single-crystal studies or very high resolution linewidth measurements) to distinguish between the resultant-field gradients at the two sites.

It is worth noting that for low-symmetry crystals (monoclinic), the principal axes for q_{lat} may depend upon the charge assignments. Therefore, in determining ground-state orbital wave functions from experimental Mössbauer data, care must be taken that the axis chosen for quantization is consistent with the PA for the crystal.

The discrepancy between Ingalls' treatment[3] of q_{lat} and the results presented here is not clearly understood. Ingalls considers the axial and rhombic components of the crystalline-field potential as a quadrupole interaction between the ferrous ion and the lattice, and derives approximate expressions relating q_{lat} and η_{lat} to the orbital-splitting parameters Δ_1 and Δ_2. Although relationships between these quantities should, in principle, exist, the calculation of such relationships may require a more sophisticated application of crystal-field theory than has been attempted as yet. In particular, the effects of neglecting higher-order axial and rhombic terms and considering only a single-orbital state are not well known. There is also some uncertainty, when using these approximations, in the correspondence between the retained terms and physical observables. These problems have been discussed in detail[23–26] for quadrupole interactions in rare-earth crystals, but definitive solutions have not yet emerged.

IV. NUCLEAR QUADRUPOLE MOMENT OF Fe^{57m}

Ingalls[3] has derived a value of 0.29 b for the nuclear quadrupole moment of Fe^{57m} by analyzing experimental Mössbauer data for $FeSiF_6\cdot 6H_2O$. Since we find that Ingalls treatment of the lattice contribution to the electric-field gradient is inconsistent with a direct lattice sum calculation and leads to an overestimation of Q, it is necessary to reanalyze the data and report the new value. We have also remeasured the magnitude of the low-temperature quadrupole splitting in $FeSiF_6\cdot 6H_2O$ and obtained 3.67 mm/sec, in good agreement with the original work of Johnson, Marshall, and Perlow.[19]

In $FeSiF_6\cdot 6H_2O$, the ferrous ion is surrounded by a trigonally distorted octahedron of water molecules. The orbital ground-state wave function is known[19,27] to be $|3z^2-r^2\rangle$, and this singlet lies lowest by an amount[28,29] $\Delta\sim 1200\ \text{cm}^{-1}$. This state produces an electric-field gradient

$$q_{val}=-\tfrac{4}{7}\langle r^{-3}\rangle,\qquad \eta_{val}=0,\tag{6}$$

and inclusion of spin–orbit coupling reduces this value by a factor[3] $[1-6(\lambda/\Delta)^2]$, where λ is the spin-orbit coupling constant ($\lambda\sim 100\ \text{cm}^{-1}$). Our estimate of the direct lattice contribution to the field gradient in this crystal is (see Table I)

$$eq_{lat}=-0.027\times 10^{14}\ \text{esu/cm}^3,\qquad \eta_{lat}=0.\tag{7}$$

By means of Eqs. (1–3), (6) and (7) and using the best values[2,3] $\langle r^{-3}\rangle=4.8$ atomic units, $(1-R)=0.68$, $(1-\gamma_\infty)=12$, and the experimentally measured[19,22] Q.S. $=-3.67$ mm/sec, we obtain for the quadrupole moment

$$Q=+0.20\ \text{b}.\tag{8}$$

Our result in Eq. (8) is substantially lower than the value derived by Ingalls,[3] the difference arising from two different sources. First, our computed lattice effect in $FeSiF_6\cdot 6H_2O$ is very small, and has the same sign as q_{val}. On the other hand, Ingalls treatment yields a lattice contribution of 12%, with a sign opposite to that of q_{val}. Second, in our calculation of Q we have neglected covalency effects, whereas Ingalls accounts for covalency by reducing $\langle r^{-3}\rangle$ by the factor $\alpha^2=0.8$. We believe that an accurate appraisal of covalency effects on the quadrupole interaction must involve a full molecular orbital treatment, as Bersohn and Shulman[18] have recently pointed out. The consideration of a covalency effect only on $\langle r^{-3}\rangle$, and not on the wave function nor the Sternheimer factors is subject to question. For example, it has been shown[30] that covalency can exist without a reduction in $\langle r^{-3}\rangle$. In the case of $FeSiF_6\cdot 6H_2O$, fortunately, the $Fe(H_2O)_6{}^{++}$ complex present in the crystal is essentially ionic,[13,16,17,31] and neglect of covalency should be a good approximation. We can crudely check this point by taking the

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effective charge on the ferrous ion to be 1.8,[31] and accounting for the four unpaired electrons of the ^5D state, one obtains $\alpha^2=0.95$ for $Fe(H_2O)_6{}^{++}$.

In further support of the above arguments, we may refer to Mössbauer studies of $Fe(H_2O)_6{}^{++}$ in hexagonal ice,[22] where analysis of quadrupole-splitting data yields the orbital ground state $|xy\rangle$, and a quadrupole moment of the same magnitude as derived above from $FeSiF_6\cdot 6H_2O$.

It is to be noted that the original study of Johnson, *et al.*,[19] which yielded the positive sign of Q, also mentioned carrying out a lattice sum on $FeSiF_6\cdot 6H_2O$, and found the contribution to be negligible. Apart from the small effects of q_{lat} and spin-orbit coupling which we have included, if Johnson *et al.*[19] had used the recent values of $(1-R)$ and $\langle r^{-3}\rangle$, they would have obtained a result essentially the same as Eq. (8).

The determination of Q from Mössbauer data has received much attention in the literature.[1,2,32–35] The original large deviation between the high value ($\sim$0.46 b) derived from Fe^{+3} ion in Fe_2O_3 [32] and the low value ($\sim$0.1 b) derived from Fe^{+2} in various crystals[19,33–35] had been reduced to a range of 0.2 to 0.3 b by better estimates of the quantities γ_∞, R, and $\langle r^{-3}\rangle$. The values we have used for these parameters are the best recent estimates obtained from unrestricted Hartree-Fock calculations,[2] and are the same as used by Ingalls.[3] It may be noted that our result $Q=0.20$ b agrees very well with that obtained from the Fe^{+3} case, which has been revised downward from 0.28 to 0.18 b.[2]

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Stopping Powers for Iodine Ions at Energies up to 200 MeV*

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Multicomponent beams of ^{127}I ions from an MP tandem accelerator have been used to extend some earlier stopping-power measurements for C, Al, Ni, Ag, Au, and UF_4 to energies up to 200 MeV. The expected maximum values of stopping powers have been reached in some cases.

REASONABLY accurate stopping-power measurements for very heavy ions in the energy range up to 100 MeV have become available only recently with the development of new accelerator techniques.[1] The results of these measurements have been useful for the analysis of data in studies of fission and in Coulomb excitation experiments; the results have an important bearing upon the design of various kinds of accelerators for very heavy ions. A collection of much of the information available on ions of medium weight has been presented by Northcliffe.[2] Theoretical analyses and comparisons with fission-fragment data were presented by Lindhard *et al.*[3] Recent measurements have been reported for Br and I ions up to energies of 100 MeV in various solid elements and compounds.[4,5]

The present work is an extension of the energy range for ^{127}I stopping powers to 200 MeV. Multicomponent beams of ^{127}I ions from an MP tandem accelerator were used.[6] Higher terminal voltages available with this new accelerator produced the increased energy range; the experimental procedure was the same as that described earlier.[4] Energy shifts between runs with and without a foil of known thickness in place were used to estimate the stopping power dE/dx, at each energy. Foils were prepared by vacuum evaporation and thicknesses were estimated from α-particle energy-loss measurements. The new dE/dx values obtained have been added to those reported earlier and the result is shown in Fig. 1. In the region of overlap (90–110 MeV) agreement with previous results was within the over-all $\pm 10\%$ uncertainty which we estimate for these measurements. For each stopping medium the data presently obtained were normalized to obtain best fits to the earlier data since the latter had been obtained with somewhat better statistics and often with more than one foil thickness; the normalization factors were, for carbon: 0.93; Ni: 0.94; Ag: 0.90; Au: 1.14; and UF_4: 1.05.

According to Lindhard *et al.*,[3] velocity-proportional electronic stopping is to be expected in the velocity region below $v_0Z^{2/3}$, where $v_0=e^2/\hbar$, and Z is the nuclear charge of the projectile. At higher velocities the ion approaches the totally stripped condition after which

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