Determination of the Nuclear Quadrupole Moment of ^{57}Fe

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We determine the nuclear quadrupole moment Q of the most important Mössbauer nucleus ^{57}Fe by comparing experimental quadrupole splittings with calculated electric field gradients (EFG) for a large number of different Fe compounds. These *ab initio* calculations are based on the linearized-augmented plane-wave band structure method. From the slope of the linear correlation between theoretical EFGs and experimental quadrupole splittings a new value of $Q(^{57}\mathrm{Fe}) = 0.16$ b is deduced, twice as large as previously suggested. Our results should also stimulate nuclear physicists to revise nuclear structure shell model calculations of Q.

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Mössbauer spectroscopy and other hyperfine interaction measurements such as nuclear magnetic resonance (NMR), nuclear quadrupole resonance (NQR), or perturbed angular correlation (PAC) are widely used experimental techniques that provide local information on the interaction of a nucleus with the surrounding electronic charge distribution. An interpretation of such measurements can lead to a detailed knowledge of the electronic and magnetic structure in a solid. One of the measured quantities, namely, the quadrupole splitting Δ_Q, is proportional to the product (of the principal component V_{ZZ}) of the electric field gradient (EFG) times the nuclear quadrupole moment Q. Since the EFG is directly related to the asphericity of the electron density in the vicinity of the probe nucleus, the quadrupole splittings allow the estimation of covalency or ionicity of chemical bonds in solids, provided Q is known.

Although Q is a purely nuclear quantity, for some isotopes these quadrupole moments are not well known. The method presented in this Letter to determine $Q(^{57}\mathrm{Fe})$ can also be applied to other nuclei and therefore has large implications on all the experimental techniques mentioned above. In addition, it can be used as reference for other methods determining Q, e.g., nuclear structure shell model calculations.

The Mössbauer isotope ^{57}Fe is probably the most frequently used nucleus for measuring hyperfine interactions. Nevertheless, its quadrupole moment is still a matter of controversy. While for a long time $Q(^{57}\mathrm{Fe})$ was believed to be in the range from 0.15 to 0.28 b, Duff, Mishra, and Das [1] found $Q = 0.082$ b by comparing Hartree-Fock calculations with Mössbauer measurements of FeX_2 molecules (X = Cl,Br) trapped in solid Ar. Subsequently, this value for Q was supported by Vajda *et al.* [2] using nuclear structure (shell-model) calculations of $Q(^{54}\mathrm{Fe})$ and the known ratio of the quadrupole splittings of ^{54}Fe and ^{57}Fe impurities in hcp Zn and Cd [3].

During the last decade EFG calculations for solids became available based on the full-potential-linearized-augmented plane-wave method (LAPW). These proved to be both accurate and reliable, which has been demonstrated for various solids including ionic insulators like Li_3N [4], Cu_2O [5], TiO_2 [6], several Hg (I) and (II) halides [7], (hcp) metals [8], and the high T_c superconductors [9]. These successful applications give us confidence that we can check and redetermine the nuclear quadrupole moment of ^{57}Fe.

In the present calculations we employ the full-potential LAPW method as embodied in the WIEN95 code [10] in a scalar relativistic version without spin-orbit coupling, which is one of the most accurate schemes for electronic structure calculations of solids. In addition to the usual LAPW basis (with a large plane-wave cutoff), we include local orbitals [11] for high lying core states—the so called semicore (SC) states—to increase the flexibility of the basis set and use a sufficiently fine k sampling.

The EFG tensor is defined as the second derivative of the Coulomb potential with respect to the Cartesian coordinates at the nucleus. The Coulomb potential is one of the crucial quantities of an accurate (full-potential) band structure calculation and in LAPW is given as lattice harmonics expansion inside the atomic spheres. In this representation the required derivatives can be determined straightforwardly [4]. A more detailed description of EFG calculations within the LAPW method can be found in Refs. [5] and [9].

Exchange and correlation effects are treated within density functional theory (DFT) using the generalized gradient approximation (GGA) [12]. Fe compounds are quite a challenge for theory, since often various magnetic interactions play an important role and different (non)magnetic phases are separated by a small energy only. An example for such a problem is the well-known failure of the standard local spin density approximation (LSDA), which predicts iron to be nonmagnetic and fcc instead of being ferromagnetic with the bcc structure. However, using GGA instead of LSDA the correct ferromagnetic bcc ground state for Fe is obtained [13] and similar improvements were found in other examples such as FeF_2 [14,15]. Because of these difficulties, we do not choose just one

Fe compound but perform calculations for the following classes of compounds: (i) The ferromagnetic (FM) metals like Fe_4N, YFe_2, Fe_2P, or FeNi. (ii) The nonmagnetic (NM) insulators FeS_2 (pyrite and marcasite) or FeSi. (iii) The antiferromagnetic (AF) Fe (III) insulator Fe_2O_3. (iv) The nonmagnetic metals $FeZr_2$ or $FeZr_3$. (v) The antiferromagnetic Fe (II) insulators FeF_2, $FeCl_2$, and $FeBr_2$.

The theoretical and experimental EFGs of these compounds are listed in Table I. The results are ordered according to an increasing EFG whose theoretical value is plotted in Fig. 1 against the experimental Δ_Q to show the excellent linear correlation. From the slope of a least-squares fit through these points we deduce a $Q(^{57}\mathrm{Fe})$ value of 0.16 b with an estimated uncertainty of about 5%. The dotted line in Fig. 1 represents the previously accepted value of $Q = 0.082$ b.

The first four classes represent compounds that are well described by band structure calculations based on DFT, since they are not highly correlated systems. In fact, we find a very good correlation between theoretical and experimental EFGs, and the remaining small differences will be discussed below. It is worth mentioning that our results are almost identical using LSDA instead of GGA.

However, the fifth class, the AF insulators $FeCl_2$, $FeBr_2$, and FeF_2 are much more challenging cases for theory, since they are strongly correlated Fe (II) compounds and their correct insulating behavior can only be obtained within GGA [14]. Consequently, the EFG depends sensitively on the choice of the exchange-correlation functional, e.g., for FeF_2 the EFG is $+6.15 \times 10^{21}$ or $+16.8 \times 10^{21}$ V/m^2 for LSDA or GGA, respectively. Nevertheless, even the EFGs of this class fall onto the regression line, and the value for Q does not change by more than 10% if one would exclude these cases from the fit.

TABLE I. Theoretical and experimental Fe EFGs in various Fe compounds including the temperature of the measurements. The experimental quadrupole splittings have been converted to EFG using $Q(^{57}\mathrm{Fe}) = 0.16$ b determined by a least-squares procedure. The experimental sign is only given when known.

Compound	Properties	V_{ZZ} (10^{21} V/m^2) Theory	Experiment
$FeBr_2$	AF insulator	-8.30	6.61^{a} (5 K)
$FeCl_2$	AF insulator	-7.60	6.01^{b} (5 K)
$FeZr_2$	NM metal	-4.40	-5.04^{c} (4.2 K)
FeS_2 (pyrit)	NM insulator	-3.47	3.66^{d} (81 K)
FeS_2 (marcasite)	NM insulator	-3.36	3.00^{d} (81 K)
Fe_4N	FM metal	-2.92	-2.58^{e} (298 K)
YFe_2	FM metal	-2.78	-2.40^{f} (15 K)
Fe_2P (3g)	FM metal	-1.13	1.20^{g} (15 K)
Fe_2P (3f)	FM metal	-0.56	0.54^{g} (15 K)
Fe_2O_3	AF insulator	$+1.99$	$+2.16^{h}$ (81 K)
FeNi	FM metal	$+2.58$	$+2.52^{i}$ (298 K)
FeSi	NM insulator	$+4.92$	4.45^{j} (4.2 K)
$FeZr_3$	NM metal	$+5.12$	$+5.53^{c}$ (4.2 K)
FeF_2	AF insulator	$+16.80$	17.12^{k} (4.2 K)

[a] Reference [21].
[b] Reference [22].
[c] Reference [23].
[d] Reference [24].
[e] Reference [25].
[f] Reference [26].
[g] Reference [16].
[h] Reference [27].
[i] Reference [28].
[j] Reference [29].
[k] Reference [30].

In the following paragraphs we discuss the sensitivity of the EFG to various parameters as well as the physical origin of the EFG for selected examples. We mentioned above an uncertainty in Q of about 5%. This might, however, stem partly from experimental difficulties such as fitting procedures or temperature effects, which can be severe especially for magnetic metals, where measurements were often done at room temperature (Table I). Such temperature effects can easily change measured quadrupole splittings by as much as 20%, e.g., in Fe_2P Δ_Q increases from 0.09 mm/s (15 K) to 0.12 mm/s (200 K) and from 0.20 mm/s (15 K) to 0.21 mm/s (200 K) at the Fe (3g) and Fe (3f) positions, respectively [16].

All theoretical values listed in Table I are calculated using lattice constants and internal parameters from experiment, except for $FeZr_3$, where only the lattice constants have been available (space group $Cmcm$; $a = 6.285$, $b = 20.764$, $c = 16.643$ a.u.) [17]. In that case, we optimize the Fe and Zr positions using forces and find for Zr in (8f) $y = 0.139$ and $z = 0.061$, for Zr in (4c) $y = 0.4155$ and $z = 0.25$, and for Fe in (4c) $y = 0.731$ and $z = 0.25$.

Since the EFG might be strongly affected by local geometries, we test for some cases the EFG dependence on internal parameters, e.g., for FeS_2, which crystallizes in two different structures, pyrite (space group $Pa3$) and marcasite ($Pnnm$). The pyrite structure consists of four Fe in (4a) and eight S atoms in (8c) with one free parameter u, which determines the S position. We optimize this coordinate $u_{\mathrm{theory}} = 0.3838$ by minimizing

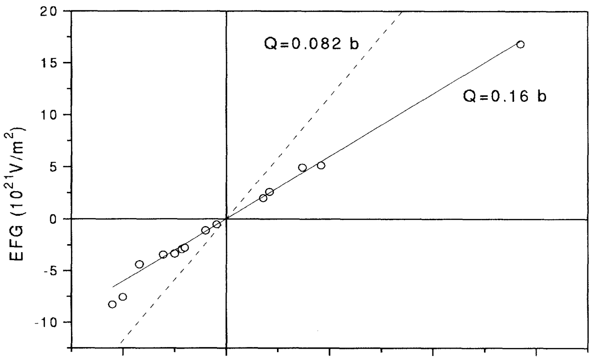

FIG. 1. Correlation between the experimental measured quadrupole splitting Δ_Q and the theoretical calculated EFG of various Fe compounds (see Table I). The full line corresponds to a least-squares fit yielding $Q = 0.16$ b, the dotted line corresponds to the previously accepted value of $Q = 0.082$ b.

the total energy and find perfect agreement with experiment [18] ($u_{\exp} = 0.384$) and two almost identical EFGs, -3.53×10^{21} and -3.47×10^{21} V/m^2 for the respective u values. In the case of marcasite the Fe position ($2a$) is fixed by symmetry, whereas there are two internal parameters for the S position [$\pm(v, w, 0;\ 0.5 - v, w + 0.5, 0.5);\ (4g)$]. Optimizing these parameters, we find reasonable agreement for the w component ($w_{\exp} = 0.378$, $w_{\text{theory}} = 0.375$), while v differs by about 2% ($v_{\exp} = 0.200$, $v_{\text{theory}} = 0.205$). The EFG increases from -3.36×10^{21} to -3.60×10^{21} V/m^2 going from the experimental to the theoretical parameters, but is still acceptable. The lattice constants have not been optimized, since their influence on the EFG is usually small and total energy calculations using GGA are within 1% of the experimental value.

The main contributions to the EFG originate from the anisotropy of the charge distribution close to the nucleus, so that often more than 90% of the EFG comes from inside the respective atomic sphere [5,9]. These contributions can be further decomposed according to different energy regions into Fe $3p$ SC and $3d$ and $4p$ valence states and the latter into p-p and d-d parts (from the product of two wave functions). Table II illustrates these terms for three selected examples.

Usually the Fe $3p$ SC-state contribution is less than 10% of the valence part except for Fe_4N (and Fe_2P), where they are opposite in sign and half the value of the valence EFG (Table II). Nevertheless, the total EFG of Fe_4N compares very well with the experimental value indicating that the SC states are treated accurately by using local orbitals (cf. discussion on rutile [6]).

In Fe_4N the p-p contribution dominates but is partly canceled by the d-d counterpart. The corresponding asphericity count

$$\Delta n_p = \frac{1}{2}(n_{p_x} + n_{p_y}) - n_{p_z} \qquad (1)$$

is –0.018 and –0.013 for spin up and spin down, respectively, indicating an excess of p_z charge, where z points towards nitrogen. This Fe $4p$-like charge can be interpreted as a reexpansion of the tails from the N $2p$ orbital tails entering the Fe sphere. The asphericity count for the d states

$$\Delta n_d = (n_{d_{xy}} + n_{d_{x^2-y^2}}) - n_{d_{z^2}} - \tfrac{1}{2}(n_{d_{xz}} + n_{d_{yz}}) \qquad (2)$$

is +0.195 (for the spin-up d states) corresponding to a depletion of d_{z^2} orbitals due to the covalent interaction with N leaving parts of the antibonding states unoccupied. Although Δn_d is significantly greater than Δn_p the much larger expectation value $\langle 1/r^3 \rangle$ of the $4p$ radial function causes this large p-p EFG contribution.

TABLE. II Main EFG contributions (in 10^{21} V/m^2) for Fe_4N, Fe_2O_3, and FeNi from semicore and valence states (for spin up and spin down) are listed together with the total theoretical and experimental values.

		Fe_4N		Fe_2O_3		FeNi	
		up	dn	upp	dn	up	dn
SC		+2.20	+1.96	−0.04	−0.38	−0.23	−0.43
Val:	p-p	−8.03	−6.39	+0.82	+0.97	+0.19	+0.23
	d-d	+6.90	+0.17	−0.39	+1.02	−0.36	+3.22
Total		−2.92		+1.99		+2.58	
Expt.		−2.58		+2.16		+2.52	

In Fe_2O_3 all contributions are well balanced, indicating an asphericity that is comparable for p and d states. FeNi consists of alternating Fe and Ni layers (CuAu structure). All spin-up contributions to the EFG are small due to the filled d shell, while the spin-down d-d contributions dominate and can be attributed to an excess of d_{xy} and $d_{x^2-y^2}$ charges ($\Delta n_d = +0.122$). This preferred occupation of the d orbitals within the Fe layer causes the positive EFG.

In summary, the present work yields $Q(^{57}\text{Fe}) = 0.16$ b, which is twice as large as found by Duff, Mishra, and Das [1] using Hartree-Fock (HF) calculations or shell-model calculations for ^{54}Fe [2], but is within the older estimates of Q. In fact, a more recent extensive theoretical HF study for FeX_2 [19] indicated that the resulting EFG is extremely sensitive to basis sets, the ground state configuration, and the Fe-X distance, so that the authors concluded that at present no reliable theoretical prediction of the quadrupole splitting for these molecules is possible. Another study based on LSDA obtained the opposite sign for the EFG in these molecules [20], indicating that one should not trust EFG calculations for such molecules. The second support for the old $Q(^{57}\text{Fe}) = 0.082$ b value consists of a combination of nuclear shell-model calculations for $Q(^{54}\text{Fe})$, perturbed angular correlation measurements on ^{54}Fe, and Mössbauer ^{57}Fe spectroscopy carried out for iron impurities in hcp Zn and Cd [2,3]. We cannot judge the reliability of this procedure, but this discrepancy to our new $Q(^{57}\text{Fe}) = 0.16$ b value needs to be resolved, and we suggest that the calculated $Q(^{54}\text{Fe})$ should be revised.

In this work we have demonstrated that EFGs in solids can be calculated from first principle using recent improvements in the description of exchange and correlation effects afforded by the GGA. Such calculations can be used together with experimentally measured quadrupole splittings to reliably determine nuclear quadrupole moments. We have proven the consistency of our results for the determination of Q by using several iron compounds with different chemical bonding and obtain a quadrupole moment of 0.16 b, twice as large as the value accepted previously.

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