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Ferrous-Ferric Anomaly in Quadrupole Moment of Fe^{57m}

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The nuclear quadrupole moment Q of Fe^{57m} has been determined from the calculated electric field gradients (including all the metal-ion–ligand overlaps) and the quadrupole splitting data in $\mathrm{Fe_2O_3}$ and $\mathrm{Al_2O_3{:}Fe^{3+}}$. The values of $Q(\mathrm{Fe}^{57m})$ obtained in the two cases are 0.180 ± 0.015 and 0.204 ± 0.018 b which are consistent with the values reported in ferrous compounds, thus disposing of the well-known ferrous-ferric anomaly.

There have been several works[1-5] which have estimated the nuclear quadrupole moment Q of Fe^{57m} by coupling the electric field gradients with the corresponding experimental quadrupole coupling constants. Though the reported values of $Q(\mathrm{Fe}^{57m})$ range from 0.1 to 0.59 b in ferric compounds,[1-4] they seem to have led to a consensus of ~0.3 b. On the other hand, the Q values[5] obtained from the ferrous data are close to 0.18 b. Attempts have also been made to reduce the gap between the two sets of results. However, the calculated values are difficult to rely upon since the overlap contributions are either completely neglected[2-4] or only considered partially.[1] Further, it has been shown[6] recently by a molecular orbital calculation on $\mathrm{Al_2O_3}$ that it is possible to obtain a very good estimate of $Q(\mathrm{Al}^{27})$. This has prompted us to perform a similar calculation on $\mathrm{Fe_2O_3}$ and $\mathrm{Al_2O_3{:}Fe^{3+}}$ to determine $Q(\mathrm{Fe}^{57m})$ and see whether the existing discrepancy in the ferrous-ferric results can be removed.

The $\mathrm{Fe_2O_3}$ and $\mathrm{Al_2O_3{:}Fe^{3+}}$ systems differ from $\mathrm{Al_2O_3}$ in the sense that there are additional orbitals ($3s$, $3p$, and $3d$ of $\mathrm{Fe^{3+}}$) which must be considered. To start with, we form, as in Ref. 6, the Hund-Mulliken-Van Vleck molecular antibonding and bonding orbitals for the complex Fe-$\mathrm{O_6}$ by taking the linear combination of the atomic orbitals $2s$, $2p$, $3s$, $3p$, and $3d$ of $\mathrm{Fe^{3+}}$, and $2s$ and $2p$ of $\mathrm{O^{2-}}$ involving only the overlap effects. Using these molecular orbitals, a many-electron wave function is constructed in the Hartree-Fock scheme. The expectation value of the field-gradient operator then gives the electronic contribution to the field gradient, q_{el}, which is separated into parts q_l, q_{nl}, q_d, and q_{dB}.[6] The total field gradient q is obtained by including the contributions from the charges on the ligand nuclei (q_n) and from the monopoles and dipoles on the remaining lattice (q_{RL}). These are not elaborated here since the details are already furnished in Ref. 6.

The expressions are simplified and evaluated[7] by use of the rotation groups to rotate the wave functions, and of the general expression[8] for Löwdin's α function to expand the functions from one center to the other. The crystal-structure parameters used for the calculations are those of Blake, Finger, and Zoltai[9] for $\mathrm{Fe_2O_3}$ and those of Newham and de Haan[10,11] for $\mathrm{Al_2O_3{:}Fe^{3+}}$. The overlap and two-center integrals are evaluated using Clementi's $2s$, $2p$, $3s$, $3p$, and $3d$ wave functions[12] for $\mathrm{Fe^{3+}}$ and Watson's $2s$ and $2p$ wave functions[13] for $\mathrm{O^{2-}}$ in a 2^+-stabilizing potential well. The calculated values of the various components of the field gradient are listed in Table I for both $\mathrm{Fe_2O_3}$ and $\mathrm{Al_2O_3{:}Fe^{3+}}$, denoting the results without the shielding factors by primes. The contributions arising from $3d$, $3p$, etc. orbitals of the $\mathrm{Fe^{3+}}$ ion are shown separately to assess their relative importance. The q_{RL}' values are deduced, as in Ref. 6, from the calculations performed by Artman and his co-workers[4,14] on the basis of monopoles and dipoles on the lattice. The total field gradient is then obtained (with appropriate shielding factors) from

$$q = (1-R)[q_l' + q_{nl}'] + (1-\gamma_\infty)[q_d' + q_{dB}' + q_n' + q_{RL}'],$$

Table I. The various electric field gradient components (in units of 10^{14} esu) in Fe_2O_3 and Al_2O_3:Fe^{3+} arising from 3*d*, 3*p*, 3*s*, 2*p*, 2*s* orbitals of Fe^{3+} as a result of overlap with the 2*s* and 2*p* orbitals of O^{2-}. Primes represent the results without shielding factors. The experimental values of eQq and the derived values of $Q(\mathrm{Fe}^{57m})$ are also listed. The uncertainties in Q are discussed in Ref. 17.

Various Components	Orbitals of Fe^{3+}	Fe_2O_3	Al_2O_3:Fe^{3+}
q'_{ℓ}	3d	0.31415	0.26097
	3p	6.39527	5.48689
	2p	0.17728	0.15849
$q'_{n\ell}$	3d	-0.64003	-0.54006
	3p	-0.10694	-0.09513
	3s	-0.08214	-0.07458
	2p	-0.03081	-0.03420
	2s	-0.01141	-0.01053
q'_{d}	3d	0.00882	0.00866
	3p	0.01649	0.01745
	3s	0.02516	0.02674
	2p	0.00005	0.00006
	2s	0.00103	0.00112
q'_{dB}		1.84987	1.43906
q'_{n}		-1.46663	-1.15445
q'_{RL}		-0.06592	0.03809
eQq(Expt.) in MHz		10.21±0.28	11.0±1.0
Q in b		0.180±0.015	0.204±0.018

where $1-R=0.68$,[15] and $1-\gamma_\infty=10.14$[3] in our cases.

Next, the use of the experimental[4,16] eQq values (Table I) yield $Q(\mathrm{Fe}^{57m})$ equal to 0.180 ± 0.015 b in Fe_2O_3 and 0.204 ± 0.018 b in Al_2O_3:Fe^{3+}, where the uncertainties in Q are determined appropriately.[17] It is gratifying[18] to note that the values of $Q(\mathrm{Fe}^{57m})$ are very close to one another. They agree with the values derived from the ferrous data,[5] thus clearing up the hitherto unexplained ferrous-ferric anomaly. Furthermore, they are consistent with the nuclear-model calculations[19] which give $Q(\mathrm{Fe}^{57m})=0.16\pm0.02$ b.

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[18] If one uses (from Table I) only that part of the overlap contribution to q that arises from the local effect of the 3*p* orbitals of Fe^{3+} in Fe_2O_3, one obtains $Q(\mathrm{Fe}^{57m})$

$=0.150$ b, which agrees with the value quoted in Ref. 1, as expected. However, if one includes also the local contributions from $2p$ and $3d$ orbitals of Fe^{3+} the value of Q is further lowered.

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Behavior of Two-Point Correlation Functions Near and on a Phase Boundary*

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The asymptotic decay of the two-point correlation function $G_{AB}(\vec{R})$ at and near a phase-separation point is discussed for d-dimensional, spin-$\frac{1}{2}$ Ising models at low temperature. The general behavior, even on the phase boundary ($H=0$), is in agreement with extended Ornstein-Zernike predictions. It is shown why the nearest-neighbor two-dimensional model in zero field is an exception. The decay of $G_{AB}(\vec{R}_1, \vec{R}_2)$ near a free surface at high temperatures agrees with phenomenological predictions using a vanishing boundary condition. At low temperature, however, the decay of correlation near a surface is exponentially slower than in the bulk.

The great utility of the Ornstein-Zernike (O-Z) and Landau-type phenomenological theories for discussing fluctuations in condensed systems is well recognized. Although these approaches generally break down in the immediate vicinity of a critical point,[1-3] the familiar prediction that the correlation function

$$G_{AB}(\vec{R}_1;\vec{R}) = \langle \hat{A}(\vec{R}_1)\hat{B}(\vec{R}_1+\vec{R})\rangle - \langle \hat{A}(\vec{R}_1)\rangle\langle \hat{B}(\vec{R}_1+\vec{R})\rangle \tag{1}$$

should decay as $e^{-\kappa R}/R^{(d-1)/2}$ as $R\to\infty$ (when $\vec{R}_1$ is far from any surfaces) is believed to be of much wider generality, at least when the operators $\hat{A}$ and $\hat{B}$ are both identified as the relevant order parameter $\hat{\Psi}$. In an earlier note[4] we examined this general O-Z hypothesis at high temperatures (considering specifically spin-$\frac{1}{2}$, d-dimensional Ising models) and demonstrated that as $R\to\infty$,

$$G_{AB}(\vec{R}_1;\vec{R}) \approx D_A^{(1)}D_B^{(1)}(e^{-\kappa R}/R^{(d-1)/2})[1+O(R^{-1})] + D_A^{(2)}D_B^{(2)}(e^{-\kappa_{ii}R}/R^{d})[1+O(R^{-1})] + \cdots, \tag{2}$$

where the inverse correlation range $\kappa=\frac{1}{2}\kappa_{ii}$ and the amplitudes $D_A^{(1)}$, etc., are dependent upon T and upon the ordering field ζ ($\equiv H$). The O-Z prediction is thus confirmed, in general, although for certain operators (containing, like the energy $\mathcal{E}$, only products of even numbers of spins) the leading "single-particle" amplitudes $D_A^{(1)}$ vanish in zero field ($H\equiv 0$), leaving the second-order or "two-particle" term as the dominant decay law.

Nevertheless doubt is cast on the general validity of the extended O-Z prediction by the exact results[5] for the two-dimensional nearest-neighbor spin-$\frac{1}{2}$ Ising models in zero field below the critical point T_c (i.e., on the phase boundary). Here the spin-spin ($G_{\psi\psi}$), spin-energy ($G_{\psi\mathcal{E}}$), and energy-energy ($G_{\mathcal{E}\mathcal{E}}$) correlation functions *all* decay as $e^{-\kappa R}/R^2$ (in place of the expected $e^{-\kappa R}/R^{1/2}$).[5] The spin-inversion symmetry is broken for all $T<T_c$ and there is no obvious reason why all the amplitudes $D^{(1)}$ should vanish [although the remaining two-particle term in (2) would then have the correct form].

In the present note, we report on a study of d-dimensional ferromagnetic spin-$\frac{1}{2}$ Ising models at *low* temperatures which answers these doubts. We show (A) that when $H\neq 0$ (i.e., "near" the phase boundary), the leading decay is always of O-Z or "single-particle" form with, however, (B) dominant corrections of the *same* form but different range parameter κ_{ii} ($\kappa<\kappa_{ii}<2\kappa$) rather than of the "two-particle" form exhibited in (2); (C) the conclusions (A) and (B) remain valid on the phase boundary, $H=0$, for all cases *except* (D) the $d=2$ nearest-neighbor Ising models where the exact results[5] are reproduced by a "two-particle" decay law; if second-neighbor interactions are introduced, the O-Z decay law is restored.[6]

As a further, more sensitive test of the general O-Z hypothesis, we have also studied the decay of correlation *near a surface*. A surface or edge of dimensionality $d_\parallel$ ($=1, 2, \cdots, d$) is defined by the incidence of $d_\perp = d-d_\parallel$ "planar" $(d-1)$-dimensional boundary "surfaces."[7] If x_α and y_α are the respective