PHYSICAL REVIEW B VOLUME 47, NUMBER 9 1 MARCH 1993-I

Dynamic-crystal-field effects on Mössbauer quadrupole splitting of Fe(II) in ferrous fluosilicate

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(Received 25 November 1991; revised manuscript received 4 August 1992)

The temperature dependence of Mössbauer quadrupole splitting of Fe(II) in ferrous fluosilicate cannot be explained on the basis of a static crystal-field interaction. The present work considers the effect of a dynamic crystal-field interaction and uses a complete set of orbital-spin-phonon basis states in order to set up the Hamiltonian matrix and compute relevant electronic observables. This formalism reproduces the experimental data reasonably well over 4.2–300 K and elucidates how vibronic effects can be handled in a simple manner.

I. INTRODUCTION

The temperature dependence of Mössbauer quadrupole splitting of Fe(II) in fluosilicates,[1] deoxyhemoglobin,[2] carbonates,[3] organometallic complexes,[4] etc., cannot be explained by the standard Ingalls approach[5] based on a static-crystal-field interaction, which is widely used to describe the magnetic properties of iron-bearing systems. The concept of a dynamic-crystal-field (or orbit-lattice or vibronic) interaction has been exploited reasonably well to explain these results in carbonates,[6,7] ferrous fluosilicate,[8] and other systems.[9] However, these initial calculations adopted a simplified model by ignoring the spin-orbit coupling or by taking its diagonal component only (that does not admix different spin states) which effectively reduces the basis states to "orbital-phonon" product states. Then a perturbation treatment was adopted to take into account the effect of orbit-lattice interaction that produces temperature-dependent admixing between otherwise orbital eigenstates derived from the static-crystal-field interaction of a given symmetry. A more consistent and rigorous approach requires that one must consider a complete set of orbital-spin-phonon basis states, set up the Hamiltonian matrix, diagonalize it to obtain eigenstates, compute expectation values of electric-field gradients, and then use them to calculate quadrupole splitting. Because the orbit-lattice interaction contains phonon annihilation and creation operators, phonon states like $|n_k\rangle$, $|n_k-1\rangle$, and $|n_k+1\rangle$ will be involved where n_k is the occupation number of phonons (with wave vector k) given by Bose-Einstein distributions at any temperature. Thus for a given orbital (Φ) and spin (M_s) state the complete set of orbital-spin-phonon basis states can be expressed as $|\Phi,M_s,n_k\rangle$, $|\Phi,M_s,n_k-1\rangle$, and $|\Phi,M_s,n_k+1\rangle$. It is obvious that for the orbital triplet of a high-spin ferrous ion in octahedral or trigonal environment there will be 45 such basis states. The formalism just mentioned has been used here to calculate the temperature dependence of the quadrupole splitting of Fe(II) in ferrous fluosilicate ($FeSiF_6$, $6H_2O$) where the disagreement between observed data and static-crystal-field calculation is very substantial (rather eye catching). It represents a refinement over our earlier work.[8]

Recently Ducouret-Cereze and Varret[10] have considered the effect of vibronic (or dynamic Jahn Teller) coupling to explain beautifully the temperature dependence of the quadrupole splitting of Fe(II) in K_2ZnF_4 and Ba_2ZnF_6. They have included all possible orbital (5) and spin (5) states along with many phonon (10) states which leads to a matrix of dimension 250. However, their approach is different (from what is being proposed in the present work) in respect of calculating vibrational matrix elements. They have used a group-theoretical (or symmetry labeled) approach to calculate nonzero vibrational matrix elements between static-crystal-field states. It may be physically valid (despite mixing caused by low-symmetry crystal-field and spin-orbit interactions) but the procedure is complex because operator (for calculating matrix elements over orbital and spin operators) and group-theoretical methods are mixed together. Also it appears that they have used 1,2,3,4,5, . . . , as the number of phonons to describe the vibrational states of the lattice whereas we believe that the number of phonons of a given energy at any temperature should follow Bose-Einstein distribution function. In another paper Varrett and Ducouret-Cereze[11] have analyzed the vibrational effects on magnetic properties of Fe(II) in K_2ZnF_4 which indicates that the energy spacings due to spin Hamiltonians are significantly changed and this in turn may get manifested in the thermal variation of magnetization. It is likely that the idea of orbit-lattice interaction will be exploited to a greater extent in the interpretation of Mössbauer, EPR, and magnetization data of iron-bearing systems and hence the matter being presented in this paper may prove complementary and useful.

II. HAMILTONIAN FOR Fe(II)

The Hamiltonian which describes various electronic interactions for a high-spin ferrous ion in a crystal is given by

$$H = H_{\rm cr} + H_{\rm so} + H_{\rm lv} + H_{\rm ol} , \qquad (1)$$

where

$H_{\rm cr}$ = crystal field interaction ,

$H_{\rm so}$ = spin-orbit interaction ,

$H_{\rm lv}$ = quantized lattice vibration Hamiltonian ,

$H_{\rm ol}$ = orbit-lattice (or dynamic crystal field) interaction .

For Fe(II) occupying a trigonally distorted octahedral site in ferrous fluosilicate one uses

$$H_{\rm cr}=B_4^0(O_4^0-20\sqrt{2}\,O_4^3)+B_2^0O_2^0+B_2^2O_2^2 \ , \qquad (2)$$

where the terms represent octahedral, axial, and rhombic field components, respectively, expressed in the standard form using Stevens[12] equivalent operators (O_n^m) and crystal field parameters (B_n^m). The dominant octahedral field splits the ^5D electronic state of a free Fe(II) ion into a lower triplet (T_{2g}) and an upper doublet (E_g) separated by $|180\ B_4^0|\sim 10^4\ \mathrm{cm}^{-1}$ which is very large. We therefore consider the lower triplet only for further calculations. The orbital eigenstates of this triplet are given by[6,12]

$$\begin{aligned}\Phi_1&=-\sqrt{2/3}\,Y_2^{-2}-\sqrt{1/3}\,Y_2^1,\\ \Phi_{-1}&=\sqrt{2/3}\,Y_2^2-\sqrt{1/3}\,Y_2^{-1}\ ,\\ \Phi_0&=Y_2^0\ ,\end{aligned} \qquad (3)$$

and they constitute orbital basis states for other interactions. The axial distortion splits the triplet into a singlet (Φ_0) and a doublet (Φ_1,Φ_{-1}) with energy difference $=|9B_2^0|$. In $\mathrm{FeSiF_6}$, $\mathrm{6H_2O}$ the orbital singlet is lower in energy. The rhombic distortion further splits the doublet with energy difference $=|8B_2^2|$. The spin-orbit interaction is given by

$$H_{\rm so}=\lambda L\cdot S=\lambda L_zS_z+(\lambda/2)(L_+S_-+L_-S_+)\ , \qquad (4)$$

where the spin-orbit coupling constant $\lambda\sim-100\ \mathrm{cm}^{-1}$. The Hamiltonian for quantized lattice vibrations is given by

$$H_{\rm lv}=\sum_k \hbar\omega_k(a_k^*a_k+\tfrac{1}{2})\ , \qquad (5)$$

where $\hbar\omega_k$ is the phonon energy, n_k is the occupation number of phonons (of wave vector k) given by Bose-Einstein distribution functions and (a_k^*,a_k) are the phonon creation and annihilation operators. The orbit-lattice (or dynamic-crystal-field) interaction, which couples the electronic and vibronic subsystems, is given by[13]

$$H_{\rm ol}=\sum_k\sum_{nm}(\hbar/M\omega_k)^{1/2}kV_n^m(L)(a_k^*+a_k)\ , \qquad (6)$$

where M is the mass of the central (Fe) atom, ω_k is the phonon frequency, k is the phonon wave vector, and $V_n^m(L)$ is an expression similar to crystal-field interactions with dynamic coupling parameters (C_n^m). In long-phonon wavelength approximations we assume that v is ω/k, where v is the velocity of acoustic phonons (i.e., sound) in the crystal.

Now we form 45 orbital-spin-phonon basis states as described earlier and then operate them on Hamiltonian (1) after dropping the dominant octahedral crystal-field term which has already been considered to obtain the orbital triplet. The matrix elements over angular momentum and spin operators are easy to calculate and they are well known. They can be nonzero between those basis states only which have the same phonon occupation number. The Hamiltonian $H_{\rm lv}$ gives nonzero matrix elements for diagonal terms only and they correspond to lattice vibrational (phonon) energy. For example,

$$\begin{aligned}\langle\Phi,M_s,n_k|H_{\rm lv}|\Phi,M_s,n_k\rangle&=\sum_k\hbar\omega_k(n_k+\tfrac{1}{2})\\&=\hbar\omega_1(n_1+\tfrac{1}{2})+\hbar\omega_2(n_2+\tfrac{1}{2})+\cdots\ ,\end{aligned} \qquad (7)$$

where $n_1,n_2,\ldots$, are the number of phonons of frequencies $\omega_1,\omega_2,\ldots$, respectively. Similarly n_k may be replaced by n_k-1 or n_k+1 for the relevant terms.

The interaction $H_{\rm ol}$ can give off-diagonal nonzero matrix elements between those basis sets which have identical spin but differ in orbital and phonon parts. For example,

$$\langle\Phi_1,M_s,n_k-1|H_{\rm ol}|\Phi_0,M_s,n_k\rangle=Q\sum_k\sqrt{\omega_k}\sqrt{n_k}\ , \qquad (8a)$$

$$\langle\Phi_1,M_s,n_k+1|H_{\rm ol}|\phi_0,M_s,n_k\rangle=Q\sum_k\sqrt{\omega_k}\sqrt{n_k+1}\ , \qquad (8b)$$

where

$$Q=(\hbar/2M)^{1/2}(1/v)\langle\Phi_1|\sum_{nm}V_n^m(L)|\Phi_0\rangle$$

and

$$n_k=[\exp(\hbar\omega_k/kT)-1]^{-1}\ .$$

Here $V_n^m(L)$ may contain in general all possible operators like $C_4^1O_4^1+C_4^2O_4^2+C_2^1O_2^1+C_2^2O_2^2$ that can give nonzero matrix elements where C's are the various dynamic-crystal-field coupling parameters. The matrix elements over operators O's can be easily obtained from standard tables.[14,15] It may be noted that operators with odd m were not present in the static-crystal-field Hamiltonian.

III. RESULTS AND DISCUSSION

In order to calculate the matrix elements over vibronic interaction one needs numerical values of phonon energy, velocity of sound, and dynamic-crystal-field coupling parameters. The lattice vibrational spectrum of any crystal may contain some discrete energy bands or it may follow the Debye model where the phonon energy is distributed over a range with a maximum cut-off. Calculated or measured lattice vibrational energy spectra for $\mathrm{FeSiF_6}$ is not available but its Debye temperature is estimated to be about 180 K.[16] Using the Debye picture one obtains the velocity of sound $v=3.9\times10^5$ cm/s which is reasonable.[8] Phonons of energy 20, 40, 60, 80, 100, and 120 cm^{-1} have been used in the present calculation, i.e., the Debye-like spectrum has been divided into six discrete phonon states. Using shorter intervals does not change the basic result except the fact that a lower value of dynamic coupling parameters is needed to obtain a similar temperature dependence of quadrupole splitting. Similarly a much larger value of dynamic coupling parameters is needed if one uses phonons of one energy only. The values of dynamic coupling parameters are not known and their relative signs can also differ. Therefore, all dynamic-field parameters have been replaced by a mean value which in effect determines the strength of the orbit-lattice coupling and it is taken as a variable. The axial splitting has been taken as 1800 cm^{-1} which is required to fit the temperature variation of quadrupole splitting in lower temperature ranges (4.2–25 K) where lattice vibrational effects are insignificant. Its value was earlier estimated to be $\sim 1500\ \mathrm{cm}^{-1}$ from the analysis of magnetic properties.[1] The rhombic splitting has been taken as zero but a small value $\sim$ a few cm^{-1} can also be used with similar results. The calculation uses $\lambda = -100\ \mathrm{cm}^{-1}$, $\langle r^{-3} \rangle = 3.563\ \mathrm{a.u.}^{-3}$ $eQ = 0.18$ b, and mean-dynamic-crystal-field parameter $= 194\ \mathrm{cm}^{-1}$. This value for the mean-dynamic-crystal-field parameter is of the same order of magnitude as the static ones which is reasonable. Huang's model[17] suggests that the dynamic parameters may be higher than the static ones by a factor $(n+1)$ and qualitatively it is in favor of the present data. The value of $\langle r^{-3} \rangle$ has been simply adjusted to match the observed and calculated quadrupole splittings at 4.2 K for a given value of nuclear quadrupole moment (eQ). Calculated and observed data are given in Table I and shown in Fig. 1. At 4.2 K the value of quadrupole splitting with or without orbit-lattice interaction remains the same as expected.

It may be noted that the electric field gradient (efg) at the Fe(2+) nucleus in a crystal arises basically from its $3d$ valence electrons,[5] polarization of $3p$ core electrons,[18] and lattice charges.[5] The first term is the most dominant. The calculations based on the local density model by Ellis *et al.*[19] and computation of molecular wave functions for $\mathrm{FeCl_2}$ and $\mathrm{FeBr_2}$ using the Hartree-Fock method by Duff *et al.*[18] are quite instructive to visualize how different electronic shells ($2p$, $3p$, $3d$) contribute to the efg and in what proportion. However, the contributions from $3p$ core electrons and lattice charges are temperature independent (unless there is a change in mean-bond length—which is not the case here) and they act as constant additives at all temperatures and hence cannot decide the nature of the ($QS-T$) curve. The nature of the ($QS-T$) curve is therefore basically determined by the thermal variation of the efg due to $3d$ valence electrons distributed over five crystal-field orbital states. Within this framework the Sternheimer shielding factor[20] and covalency factor (which effectively reduces the value of $\langle r^{-3} \rangle_{3d}$) appear as constant multipliers to the expression for efg and they determine the magnitude of QS but not the nature of its temperature variation. Even the measurement of QS at one temperature cannot indicate if vibrational interactions are important because there is no way to know how much change in QS has been produced by the vibrational effects. However, if the QS versus T study is made, one can recognize the failure of the static-crystal approach and then consider the dynamic-crystal model.

TABLE I. Temperature variation of quadrupole splitting (QS). Theor-I: calculated without dynamic-crystal-field interaction. Theor-II: calculated with dynamic-crystal-field interaction. Experimental data taken from Ref. 1.

T (K)	QS (mm/s) (Expt)	QS (mm/s) (Theor-I)	QS (mm/s) (Theor-II)
4.2	−3.608	−3.608	−3.608
25	−3.622	−3.626	−3.625
50	−3.627	−3.633	−3.627
77	−3.624	−3.636	−3.622
100	−3.617	−3.638	−3.614
150	−3.586	−3.639	−3.586
200	−3.544	−3.640	−3.543
250	−3.485	−3.640	−3.482
300	−3.398	−3.639	−3.400

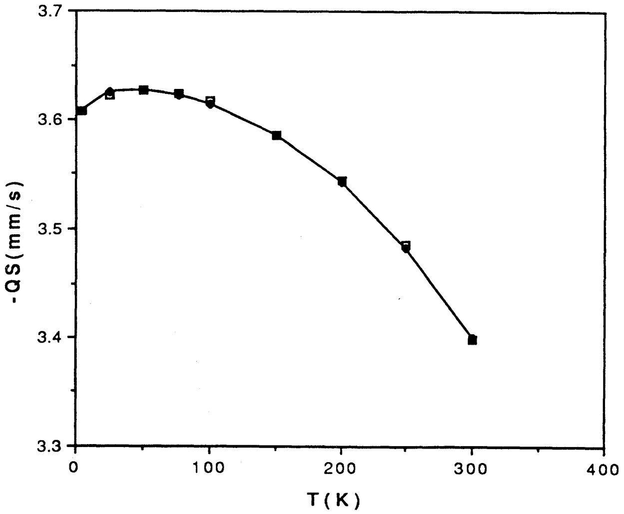

FIG. 1. Quadrupole splitting of Fe(II) in $\mathrm{FeSiF_6, 6H_2O}$. Experimental data (open squares) and calculated values (solid circles) using dynamic-crystal-field interaction are plotted. They almost superimpose.

The form of the orbit-lattice (or dynamic-crystal field) interaction given in expression (6) is convenient to use along with other interactions (expressed in terms of orbital and spin operators) in order to set up the complete Hamiltonian matrix. Often normal coordinate analysis for a molecule is done to obtain vibronic wave functions and allowed frequencies, but it is mostly used to understand the symmetry property of the combined electronic—vibronic wave function in order to explain some electronic transitions which are normally not allowed under Laporte selection rule but get permitted due to vibrational admixture.[21] This approach is suitable for a qualitative understanding of the observed electronic transitions (or bands) from transition metal ions in a crystal but not appropriate for a quantitative analysis when one desires to set up a complete Hamiltonian matrix in terms of orbital-spin-phonon basis states. It might be relevant to note that the orbit-lattice interaction depends upon relative displacement between the central Fe ion and its ligands, and it simulates the modes of vibration for an MX_6 cluster. The process does not correspond to a simple change in the mean-bond length rather it represents a harmonic displacement of the central ion relative to its ligands. This produces lattice waves (phonon spectrum) and modulation of 3*d* electronic charge cloud due to change in the Fe-ligand distance at any time.[12] The present work uses the Debye model of phonon spectrum. The consideration of local modes of vibration may be more appropriate but it requires a detailed knowledge of the same. However, the basic formalism will remain unchanged except that one will have to include only those phonon frequencies which are consistent with local vibrational modes.

This calculation uses basically three variable parameters—the trigonal field splitting, Debye temperature (the velocity of acoustic phonons is related to it), and the mean-dynamic-field parameter—which decide the nature of the $(QS-T)$ curve. The crystal-field-energy separation of 1000 to 2000 cm^{-1} is too small to be measured directly through optical absorption spectroscopy and these are usually estimated from the magnetic property data. The earlier estimate of trigonal field splitting from magnetic data is similar to the value and used here. The Debye temperature is also a measured parameter. Thus the mean-dynamic-field parameter, which couples electronic and vibronic states, is the only variable parameter in a true sense and this makes the calculations more realistic. There is no way to determine this parameter directly.

The inclusion of orbit-lattice interaction reproduces quite well the temperature dependence of quadrupole splitting of Fe(II) in ferrous fluosilicate over 4.2–300 K which is otherwise not possible on the basis of static-crystal-field calculations (shown in Table I). Phonons of low energy are found to be more effective in reducing the value of quadrupole splitting. This is consistent with the fact that at any temperature low-energy phonons are more abundant to produce coupling between ground and excited crystal-field orbitals.

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