

## 3d Charge Density Distribution and Crystal Field in FeCl<sub>2</sub>: A Mössbauer Study\*

Y. HAZONY

*Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08540*

AND

HANG NAM OK†

*Solid State and Materials Laboratory, Princeton University, Princeton, New Jersey 08540*

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Available Mössbauer quadrupole-splitting (QS) data for FeCl<sub>2</sub> are analyzed in terms of crystal field and covalency parameters. It is shown that the temperature variation of QS in the paramagnetic phase is consistent with a large expansion of the 3d electronic charge density distribution ( $\alpha^2 = \langle r^{-3} \rangle / \langle r^{-3} \rangle_0 \approx 0.4$ ) as was previously predicted from the systematics of QS and isomer shift in the halides. The analysis yields a large ratio of 8.4 between the trigonal field component and the spin-orbit coupling constant, which is consistent with the Ising model proposed by Kanamori for the low-temperature magnetic properties of FeCl<sub>2</sub>.

RECENTLY, Axtmann *et al.* have performed Mössbauer studies on three series of high-spin ferrous compounds: the anhydrous ferrous halides,<sup>1</sup> the hydrates of FeCl<sub>2</sub>,<sup>2</sup> and the hydrates of FeI<sub>2</sub>.<sup>3</sup> In these studies the authors observe that, apart from a magnitude factor, the temperature-dependence curves of the quadrupole splittings (QS) above the respective magnetic transition temperatures are very similar for all these compounds. Since the QS magnitude factors are linearly related to the covalency factors  $\alpha^2 = \langle r^{-3} \rangle / \langle r^{-3} \rangle_0$ ,  $\alpha^2$  values of 0.75, 0.6, 0.42, 0.39, and 0.34 have been derived for Fe(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>, FeF<sub>2</sub>, FeCl<sub>2</sub>, FeBr<sub>2</sub>, and FeI<sub>2</sub>, respectively. Such small values for  $\alpha^2$  mean large expansion of the 3d electronic wave functions with respect to those of the free ion. Although in the right order of covalency and in consistency with the nephelauxetic series,<sup>4</sup> the numbers for the heavier halides are rather small in comparison with what is generally accepted in the Mössbauer literature, as is reflected by the conflict with the results of Ono *et al.*<sup>5</sup> These authors have measured the Mössbauer spectra of Fe<sup>57</sup> in FeCl<sub>2</sub> over the temperature range 1.5–530°K, and analyzed the temperature dependence of QS in terms of crystal field theory. In their calculation the binding of Fe<sup>2+</sup> to its neighboring ligands was assumed to be highly ionic (covalency factor  $\alpha^2 \sim 0.9$ ). Comparison with Tinkham's estimate of the covalency factor for FeF<sub>2</sub> ( $\alpha^2 \sim 0.6$ )<sup>6</sup> and with Owen's value for Fe(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> ( $\alpha^2 \sim 0.8$ )<sup>7</sup> would imply that FeCl<sub>2</sub> is more ionic than FeF<sub>2</sub> and Fe(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>. Suchet and Bailly<sup>8</sup> calculated

"ionicity" parameters for FeF<sub>2</sub>, FeCl<sub>2</sub>, FeBr<sub>2</sub>, and FeI<sub>2</sub> from thermochemical data and the crystalline arrangements of these compounds. They obtained "ionicity" values of 0.88, 0.71, 0.53, and 0.35, respectively, which are consistent with the traditional concepts of covalency and favor the interpretation of the Mössbauer results by Axtmann *et al.* over that of Ono *et al.* The latter also obtain a small energy separation ( $\Delta = 119$  cm<sup>-1</sup>) between the orbital doublet and the orbital singlet. This separation is comparable to their value for the spin-orbit coupling constant ( $\lambda = 95$  cm<sup>-1</sup>). These parameters give a lower group of three closely spaced spin-orbit states separated by an energy of 172 cm<sup>-1</sup> from the next spin-orbit states.<sup>5</sup> Within such an energy-level scheme, an Ising model which is based on a lower doublet is not a good approximation for the low-temperature magnetism in FeCl<sub>2</sub>.

Kanamori<sup>9</sup> has investigated the magnetic properties of FeCl<sub>2</sub>. Assuming that the lowest orbital state of the ferrous ion in the crystalline field of trigonal symmetry is a doublet and that it is well separated in energy from the singlet, as compared with the spin-orbit coupling energy, he could explain the behavior of the magnetic susceptibility of FeCl<sub>2</sub>. Taking into account the spin-orbit coupling, the lowest state becomes a doublet separated from the next level by an order of the spin-orbit coupling constant. He concluded, therefore, that at low temperatures, a good approximation to the magnetic properties of Fe<sup>2+</sup> in FeCl<sub>2</sub> is an Ising model in which the transverse spin components are completely quenched. Yomosa<sup>10</sup> and Heap<sup>11</sup> adopted this model and applied the Bethe-Peierls statistical method to calculate a number of properties.

Jacobs and Lawrence<sup>12</sup> analyzed two measurements of the temperature dependence of the sublattice magnetization of FeCl<sub>2</sub>. One is from neutron diffraction measurements obtained by Wilkinson *et al.*<sup>13</sup> and the

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† Present address: Department of Physics, Yonsei University, Seoul, Korea.

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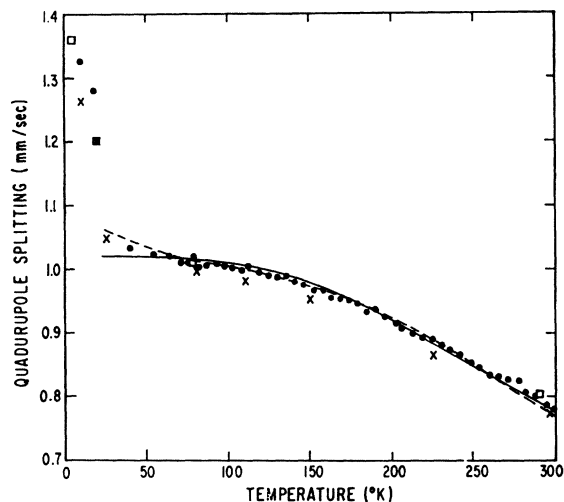


FIG. 1. Temperature dependence of the quadrupole splitting in  $\text{FeCl}_2$ . Experimental: ●, Ref. 3; □, Ref. 5; ×, Ref. 15. Theory: solid curve, present results; dashed curve, Ono *et al.* (reproduced from Ref. 15).

other is from  $\text{Cl}^{35}$  nuclear magnetic resonance, below  $T_N$ , obtained by Jones and Segel.<sup>14</sup> They showed that the temperature dependence of the normalized sublattice magnetization is reasonably described by an Ising model in the Bethe-Peierls approximation.

Recently, Johnson and Dash<sup>15</sup> remeasured the Mössbauer QS and found considerable deviation between their experimental values and the theoretical curve obtained using the parameters of Ono *et al.*

It is instructive, therefore, to know whether, applying crystal field theory to the  $3d$  delocalization model of Axtmann *et al.*, one can satisfactorily predict the temperature dependence of QS in  $\text{FeCl}_2$ , and whether the resulting energy-level scheme favors the Ising model at low temperatures.

The energy separation between the  $T_{2g}$  and  $E_g$  levels of  $\text{Fe}^{2+}$  ion in  $\text{FeCl}_2$  crystal due to the octahedral coordination was found to be about  $7000 \text{ cm}^{-1}$ .<sup>16</sup> The contribution of the  $E_g$  level to the electric field gradient is therefore negligible at ordinary temperatures and will be ignored in the present discussion. Taking the quantization axis along the trigonal axis, the three  $t_{2g}$  orbital wave functions can be written<sup>17,9</sup>

$$\begin{aligned}\psi_1 &= \left(\frac{2}{3}\right)^{1/2} Y_2^{-2} + \left(\frac{1}{3}\right)^{1/2} Y_2^1, \\ \psi_0 &= Y_2^0, \\ \psi_{-1} &= \left(\frac{2}{3}\right)^{1/2} Y_2^2 - \left(\frac{1}{3}\right)^{1/2} Y_2^{-1},\end{aligned}$$

where  $Y_2^m$  ( $m=0, \pm 1, \pm 2$ ) represent the spherical harmonics of the second order.

In a trigonal field, the  $T_{2g}$  level splits into a singlet ( $\psi_0$ ) and a doublet ( $\psi_1, \psi_{-1}$ ). The interaction Hamiltonian for the  $T_{2g}$  electron may be written as a  $15 \times 15$  matrix of the form  $-\frac{1}{3}\Delta(3L_z^2 - 6) + \lambda \mathbf{L} \cdot \mathbf{S}$ , where  $\Delta$  is the energy separation between the orbital singlet and orbital doublet due to the trigonal crystal field and  $\lambda \mathbf{L} \cdot \mathbf{S}$  represents the spin-orbit coupling. If thermal relaxation times between the 15 eigenstates of this Hamiltonian are shorter than the quadrupole relaxation time, then the QS is determined by a thermal average of the contributions of the 15 levels, and may be written as<sup>18</sup>

$$\Delta E(T) = \Delta E_0 \alpha^2 F(\Delta, \alpha^2 \lambda_0, T),$$

where  $\Delta E_0 = (2/7)e^2 Q(1-R)\langle r^{-3} \rangle_0 = 5.5 \text{ mm/sec}$  was chosen following Ingalls,<sup>18</sup> the spin-orbit coupling constant  $\lambda$  is related to that for the free ion by  $\lambda = \alpha^2 \lambda_0$  ( $\lambda_0 \sim 100 \text{ cm}^{-1}$ ), and  $F$  represents the thermal average over the 15 energy levels.

Fitting the theoretical QS( $T$ ) curve to the available experimental results above  $T_N$ <sup>3</sup> (Fig. 1), we find  $\alpha^2 = 0.4$  and  $\Delta = 8.4|\lambda| \sim 340 \text{ cm}^{-1}$ . Since  $\Delta$  is much larger than  $|\lambda|$ , the energy-level scheme is such that the ground state is a doublet and the spin of  $\text{Fe}^{2+}$  can be described in an Ising model as proposed by Kanamori.<sup>9</sup>

With the above parameters ( $\alpha^2 = 0.4$  and  $\Delta = 8.4|\lambda|$ ), the wave functions for the ground doublet are

$$\begin{aligned}\phi_+ &= 0.982\psi_{-1}\chi_2 - 0.150\psi_0\chi_1 - 0.117\psi_1\chi_0, \\ \phi_- &= 0.982\psi_1\chi_{-2} + 0.150\psi_0\chi_{-1} - 0.117\psi_{-1}\chi_0,\end{aligned}$$

where  $\chi_j$  ( $j=0, \pm 1, \pm 2$ ) are the spin-wave functions of  $\mathbf{S}=2$ . The magnetic moments of these two states are

$$\langle \phi_{\pm} | 2\mathbf{S}_z + L_z | \phi_{\pm} \rangle \mu_B = \pm 4.85 \mu_B,$$

where  $\mu_B$  is the Bohr magneton.

At temperatures below  $T_N$  the ground doublet will split by the exchange interaction. In the molecular-field approximation, the exchange interaction term may be written as  $-2Jx\langle \mathbf{S}_z \rangle \mathbf{S}_z$ , where  $J$  is a molecular-field constant,  $x$  is the number of nearest neighbors, and  $\langle \mathbf{S}_z \rangle$  is the thermally averaged value of  $\mathbf{S}_z$ . Since  $\phi_+$  and  $\phi_-$  are essentially equal to  $\psi_{-1}\chi_2$  and  $\psi_1\chi_{-2}$ , respectively, they are, to a good approximation, energy eigenstates of  $-2Jx\langle \mathbf{S}_z \rangle \mathbf{S}_z$ .<sup>19</sup> Therefore, the magnetic moment at liquid-helium temperatures is  $4.85 \mu_B$ . The available experimental value of  $4.5 \pm 0.7 \mu_B$ <sup>13</sup> is not accurate enough to distinguish between the present result and the value of  $4.17 \mu_B$  obtained from the model of Ono *et al.*<sup>5</sup>

The strong evidence for a large low-temperature anharmonicity in  $\text{FeCl}_2$ <sup>3,15,20</sup> indicates that one should also consider contributions from the temperature variation of crystal field components, magnetostrictive terms

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in the magnetic interaction, as well as a possible first-order phase transition. Any of the three effects or a combination of them can explain the  $QS(T)$  anomaly below  $T_N$ ; however, there are not enough experimental data available at present time for a meaningful discussion of this problem.<sup>21</sup>

<sup>21</sup> A still unexplored mystery of this phase transition is the vanishing magnetic field at the iron nucleus below  $T_N$ . The discussions of the "residual" field in Refs. 5 and 15 are based on an observed line broadening below  $T_N$ . The results reported in Ref. 3 show evidence for strong thermal hysteresis. In the experiment shown in Fig. 1 the spectra at 10 K showed a symmetric doublet, the linewidth of which reduced from an initial value of 1.2 to 0.4 mm/sec after about 8 h. In the following warmup the linewidth reduced continuously to 0.27 mm/sec at room temperature with no significant change at  $T_N$ . Unlike Ref. 15, the spectrum was clean of traces of the monohydrate, while in the spectra shown in Ref. 5 such traces would not have been resolved.

The purpose of the present work was to reaffirm the conclusion of Axtmann *et al.*<sup>1-3</sup> that there is a strong radial expansion of the  $3d$  electronic wave functions in solid ferrous compounds due to covalency effects. We have demonstrated that Mössbauer  $QS(T)$  data are too simple to allow for a unique determination of crystal field parameters. The present results are consistent with the traditional concepts of covalency in the halides as well as with the Ising model for the magnetic behavior at low temperatures.

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## Photoemission Studies of the Alkali Metals. I. Sodium and Potassium\*

NEVILLE V. SMITH† AND WILLIAM E. SPICER  
Stanford University, Stanford, California 94305  
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Measurements have been made of the photoelectric yield and the photoelectron energy distribution curves (EDC's) on Na and K in the photon energy range 2.3–11.6 eV. The samples were thick films prepared by evaporation onto various substrates in a specially constructed ultrahigh vacuum chamber. The results are interpreted in terms of a model which assumes that each of the three stages of the photoemission process—optical excitation of electrons, transport to the surface and escape across the surface—may be treated independently. The most noteworthy feature of the frequency dependence of the photoelectric yield, expressed in electrons per incident photon, is a sharp drop on passing through the plasma frequency. It is shown that this may be understood in terms of the rapid variations of the optical constants in this region. The EDC's are characterized by a pronounced peak at the high-energy edge which is identified as arising from primary or unscattered electrons. Its width is found to increase with increasing photon energy, an effect which can be understood in terms of the direct (or  $\mathbf{k}$ -conserving) nature of the optical transitions. The simple theory of direct transitions in a nearly free-electron metal is expounded, and the form of the EDC is derived. It is predicted that the optically excited electrons should originate from initial states which are distributed uniformly between a maximum energy equal to the Fermi energy  $E_F$  and a minimum energy  $E_{\min}$  which varies quadratically with photon energy. In the experimental range, the width  $E_F - E_{\min}$  is predicted to increase with photon energy, in agreement with the observed behavior. However, the predicted shape of the EDC's is rectangular, whereas the observed shape is more triangular. The other main feature of the EDC's is an abundance of electrons at energies below the leading peak. These are identified as electrons which have undergone an inelastic scattering due to electron-electron interactions before emerging from the metal. This region of the EDC may be regarded as a kind of characteristic energy-loss spectrum. Na shows a single, rather wide low-energy peak in this region. K shows a narrower low-energy peak and a broad intermediate bump identified as a plasmon energy loss. This intermediate bump has been seen also in preliminary work on Rb and Cs, and is found to become more pronounced and closer to the leading peak. The systematic trends therefore support the plasmon interpretation. The energy separation of the peaks is more consistent with a surface rather than a volume plasmon loss. The structure identified as plasmon energy loss is, however, superimposed on a large background, which is attributed to energy loss by pair creation. Rough estimates of the relative proportions indicate that pair creation dominates plasmon creation as the main scattering mechanism.

### I. INTRODUCTION

THE alkali metals form an ideal system for the fundamental investigation of photoemission. Their band structures are believed to be simple, so

that the predictions of conventional theory may be easily worked out and tested. Scattering due to electron-electron interactions plays an important part in through the Center for Materials Research at Stanford University and by the National Science Foundation.

† Present address: Bell Telephone Laboratories, Murray Hill, N. J. 07971.

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