CHARGE DISTRIBUTION AND COVALENCY EFFECTS

ON MOSSBAUER PARAMETERS IN KFeS$_2$

by

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ABSTRACT

In this paper we report the effects of covalency on the Mössbauer Hyperfine parameters in KFeS$_2$. Using the point charge model, constrained by the charge neutrality condition and the experimentally determined quadrupole doublet separation, we determine the ionic character of the atoms in the crystals. These values are further compared and discussed with ionic character estimates from Isomeric Shift (Modified WWJ Plot) and other methods based on electronegativity differences. The previous Mössbauer spectroscopic work is also extended to liquid nitrogen temperature. It has been shown, how the simple concept of electronegativity difference can also account for the order of magnitude of the magnetic field. The angle between magnetic field direction and field gradient is also deduced.

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I. INTRODUCTION

The importance of considering the effects of covalency on the Mössbauer hyperfine coupling constants have been often[1-5] emphasized. In this paper we study these effects in $KFeS_2$ crystals formed at high temperatures by fusion, having iron in covalent tetrahedral bonds with sulphur. Mössbauer spectroscopic studies of this compound by Kerler et al[6] and by Raj & Puri[7] indicated small isomer shift and temperature independent quadrupole splitting values, in the range characteristic of the trivalent state with high spin configuration[8], and a magnetic field reported to be less than one half the theoretical free ion value, which we have correlated with the covalent character of the Fe-S bonds.

This covalent character is expected in view of the small electronegativity difference between sulphur and iron, which should result in an even redistribution of charges in the crystal in accordance with the principle of electronegativity equalization[9,10].

We are particularly interested in estimating this charge transfer in order to study more closely the covalent character of the bonds and their effects on the Mössbauer hyperfine fields.

Since iron in $KFeS_2$ is supposedly in a $^6S_{5/2}$ spherosymmetrical charge state, the point charge model[11], is a reasonable approximation for determining the electric field gradient at the nuclear site, which should arise solely from charges external to the Fe^{3+} atom either by direct contribution or by indirect core polarization.

The EFG tensor is obtained from direct lattice calculations carried out on an IBM-360 computer and the effects of covalency were incorporated by placing effective charges[12] at the lattice sites.

We then determine the charge distributions of the $(FeS_2)^{-1}$ complex

ions required to produce the observed field gradients at the Fe nucleus and compare the rsultant charges with those estimated using the isomer shift calibration (Modified WWJ Plot)[1].

Analysis of the liquid nitrogen asymmetric Mossbauer spectrum yields the hyperfine interaction constants and their relative orientations. The effective charges are compared with independent estimates for other sulphides[13-15] and the hyperfine field is correlated with electronegativity difference and covalency as suggested by Watson & Freeman[5] and others[14].

II. CRYSTAL STRUCTURE

$KFeS_2$ is a monoclinic crystal[15], with space group symmetry C_{2h}^6 with 4 molecules per unit cell having all Fe at equivalent sites.

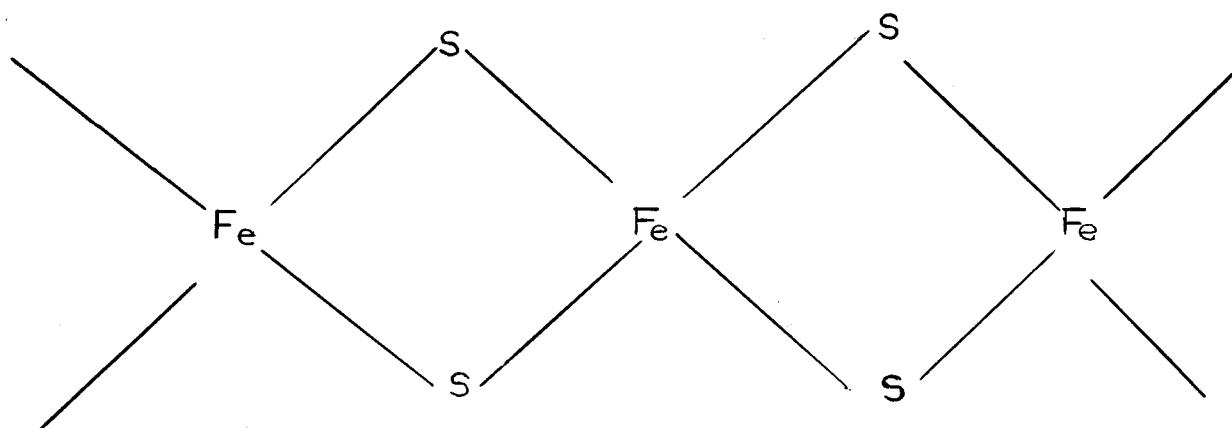The iron atoms are principally covalently bonded by sulphur tetrahedra $(4s4p^3)$.

Fig. 1

The $(FeS_2)^{-1}$ ions are arranged in chains of FeS_4 tetrahedra which account for the fibrous character of the substance and suggest a strong covalent bonding for iron atoms which are arranged in chains along the c axis.

III. EXPERIMENTAL

$KFeS_2$ are permanganate coloured needle shaped monoclinic crystals, prepared[16] by fusing iron powder with potassium carbonate and sulphur, and leaching the cold product in water.

The Mössbauer spectra of polycristalline sample were recorded in the standard transmission geometry with a constant acceleration doppler velocity transducer, 400 multichannel and Co^{57} in Cu matrix with an initial activity of 25 mCi. Due to the very fibrous nature of these crystals, there is a slight asymmetry in the line intensities of our spectra as may be observed in Fig. 2.

IV. CALCULATIONS OF EFFECTIVE CHARGES USING POINT CHARGE MODEL

Using Boon's[15] proposed bonding structure $K^+(Fe-S_2)^{-1}$ for this compound we assign charges plus one to the potassium ions and a wide range of charges to the sulphur atoms and determined the corresponding effective charges on iron necessary to mantain charge neutrality. Using the available crystallographic data[15], the values of the EFG tensor from charges only were computed from the following lattice sum:

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

where e_k and (R_{xk}, R_{yk}, R_{zk}) are the effective charges and the coordinates of the k th atom in an arbitrary orthogonal coordinate system.

We considered the contribution from all lattice sites within a sphere of 50 Å enclosing the iron nucleus. The EFG tensor thus obtained was diagonalized and the principal values of V_{ij} were designated according to the

convention that $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$, $eq = V_{zz}$ & $\eta = (V_{xx} - V_{yy})/V_{zz}$.

Variations in the values of V_{zz} for spherical shells between 40 $\overset{o}{A}$ and 50 $\overset{o}{A}$ inclusive were of the order of 0.1 - 0.3% and hence ensured a good convergence. This procedure was repeated for all charge distributions.

Using the latest reported values of 1.87[17] barns and $- 9.14$[18] for quadrupole moment Q and antishielding factor γ_∞ respectively, the Mössbauer gamma-line doublet separation is then obtained from the expression:

$$\Delta E_Q = 1/2 \ e^2 \ q \ Q \ (1 - \gamma_\infty) \ (1 + \eta^2/3)^{1/2}$$

for each charge distribution.

In view of the temperature independent quadrupole splitting characteristic of the trivalent spherosymmetrical charge state, we assume the 4p character obtained by the iron atoms in the redistribution process as equally divided in all the three p (px, py, pz) orbitals and in conformity with the Townes and Dailey[4] approximation, we have neglected any possible contribution from these overlapping orbitals.

As indicated in Fig. 3 the quadrupole doublet separation in mm/sec versus effective charge yields a best fit with our experimentally obtained value of 0.53 ± 0.02 mm/sec when we assign charges* of approximately -1.3 and 1.6 to sulphur and iron atoms respectively.

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* Throughout this paper, charges are expressed in units of electron charge.

Fe and S, (Fig. 1), have tetrahedral bonding $(4s4p^3)$. The WWJ Plot indicates a 0.35 - 4s contribution[7] from the sulphur ligands. Assuming each bond as equivalent the Fe atom receives a charge of 0.35 from each sulphur which yields effective charges 3. $- 0.35 \times 4 = 1.6$ for Fe and $- 1.3$ for S. These values are in agreement with those obtained from our point charge model.

Further analysis of Fig. 3 indicates that the quadrupole doublet separation is directly proportional to the ionic character of the crystal's atoms, increasing linearly with increase in ionic character. The experimental value is reduced to approximately one half of the expected idealy ionic value.

The afore-mentioned linear relationship is a direct consequence of the redistribution of charges in the $(Fe-S_2)^{-1}$ ions constrained by the charge neutrality condition and the reduced value of quadrupole splitting can be attributed to the reduction of the formal charges of the atoms.

• It is interesting that the values of Q.S., Magnetic Field and isomer shift corresponding to iron in $KFeS_2$ appear to be approximately one half the magnitude expected for the free ion values. Thus there appears to exist a simple correlation between the reduced hyperfine structure constants and the ionic character of Fe atom, as reflected in the effective charges, which are roughly one half the formal +3 free ion charge.

Although our point charge model calculations of ionic character for $KFeS_2$ are also substantiated by calculations in progress[19] for a series of similar compounds, we shall nevertheless make other supporting independent estimates of ionic character for $KFeS_2$ and comparisons with other sulphides, using different models based on electronegativity differences. These models, as will be demonstrated, can also be advantageougly used for calibrating the effective charges and spread of the hyperfine fields in a variety of hosts.

V. CORRELATIONS OF IONIC CHARACTER AND CALCULATIONS OF EFFECTIVE CHARGES BASED ON ELECTRONEGATIVITY DIFFERENCES

X-Ray studies were also performed by Boon[15] on $NaCrS_2$ and on comparing the nature of the Fe-S and Cr-S bonds he proposed a more covalent character for $KFeS_2$.

Peterson et al[16] determined the charge distributions in α-$NaFeO_2$ type crystals, using point charge model calculations constrained by the ^{23}Na nuclear quadrupole coupling constants obtained by NMR and found a linear relationship connecting the effective charges of the metals in these compounds with the electronegativity differences of the metal ligand neighbor bonds.

The effective charge for iron in $KFeS_2$, estimated from this linear relation is about 1.6 and is in close agreement with that obtained from point charge model.

The effective charges calculated for Cr in $NaCrS_2$ is 2.08 and for In in $NaInS_2$ is 1.63.

The lower values of effective charge for Fe in $KFeS_2$ as compared to that of Cr in $NaCrS_2$ suggest that the Fe-S bonds are more covalent in character than the Cr-S bonds, in agreement with Boon's proposal.

Using a completely different approach, i.e., relative strengths of hyperfine splitting obtained from paramagnetic resonance, Van Wierengen[14] estimated 0.7 ionic character for Mn^{2+} with sulphur ligands. The ionic character of iron in $KFeS_2$ is $1.6/3.0 = 0.533$. Since ionic character is a function of electronegativity difference (E.D.)[9,10,18] , these two independent results can also be correlated, i.e., one can estimate the ionic character of Fe in $KFeS_2$ by calculating the proportional changes of ionicity through

electronegativity differences.

Using the models of Pauling and Hannay & Smyth[9] with due allowance for the coordination numbers & the electronegativity values listed in Table I, we have thus estimated the ionic character for Fe (Table II).

Similar estimates were made using the values of ionic character reported for $NaCrS_2$ and $NaInS_2$.

These estimates lie in the range from 56% to 68% and thus compare satisfactorily with the 53.3% ionic character determined from point charge model calculations and the modified WWJ Plot.

Ferreira[10] has also suggested a model for determining the charge transfer in complex molecules which in addition to electronegativity differences and coordination numbers also takes into account the principles of equalization of effective electronegativities and electronic screening constants.

This model was used by J. Danon[1] for determining charge transfer while recalibrating the WWJ Plot and will provide us another independent estimate of effective charges in $KFeS_2$.

Following the notation used in Ferreira's paper[10] and the suggested bonding structure[15] for $KFeS_2$ the effective charges and ionic character of Fe in this compound are obtained as follows.

The estimated values[10] of $\Delta X_i^+ = 0.2508$ & $\Delta X_j^- = 0.2310$ are used in equations:

$$X_B(E) = X_B(0)_e + q \sum_{i=1}^{m} \Delta X_i^+ \quad , \quad X_A(E) = X_A(0)_e - q \sum_{j=1}^{n} \Delta X_j^-$$

$$\text{and} \quad q = \frac{X_B(0)_e - X_A(0)_e}{\sum_{i=1}^{m} \Delta X_i^+ + \sum_{j=1}^{n} \Delta X_j^-} \qquad \text{from which we obtain an effective charge}$$

transfer of 0.36 from each sulphur ligand. This results in an effective charge of 1.56 for Fe atoms which corresponds to 52% ionic character for iron and is in very good agreement with our previous estimates.

Thus, the varying ionic-covalent character of complex compounds are well accounted for when we consider the electronegativity differences of the metal-ligand neighbor bonds, which suggest that these models based on electronegativity differences may also be used to account for the spread of Mössbauer hyperfine parameters.

VI. ANALYSIS OF THE MÖSSBAUER SPECTRA AT LOW TEMPERATURE

Analysis of the combined quadrupole and magnetic split spectrum at liquid nitrogen temperature (Fig. 2) yields[21] for isomer shift and magnetic field values of 0.27 ± 0.02 mm/sec (w.r.t iron) and 215 ± 5 Kgauss respectively, which are in agreement with the saturation values extrapolated from the work of Kerler et al[6] .

If we neglect the small asymmetry parameter in $KFeS_2$, the angle between the internal magnetic field and the symmetry axis of the EFG tensor can be determined from the relation

$$(3 \cos^2 \theta - 1) = 8 \, \varepsilon / e^2 \, qQ$$

where $\quad \varepsilon = 1/2 \left[1/2(L1 + L6) - 1/4(L2 + L3 + L4 + L5) \right]$

and the Li's are the line positions in Fig. 2 in increasing order from left to right.

Using the value of $1/2(e^2 \, q \, Q)$ as the quadrupole doublet separation, the solution of this equation yields for the angle θ a temperature independent value of $20 \pm 5^{\circ}$.

The estimated value of 215 Kgauss in $KFeS_2$ is however very small compared to 630 Kgauss corresponding to the Fe^{3+} free ion, determined by Watson and Freeman[5], using exchange polarized Hartree Fock calculations via the Fermi contact term.

The spread of hyperfine fields (H.F.) for $^6S_{5/2}$ state ions in a variety of host have been thoroughly discussed in the literature[5,14,22-27].

Various models have been proposed to account for the reduced values of these fields often[26-31] observed, and the interpretation usually given is that the H.F. depend on covalent bonding, the more covalent the bonds the smaller the observed H.F. values.

Using models based on electronegativity differences the spread of these hyperfine fields have been correlated with the covalent-ionic character of the bonds[26,27].

These correlations suggest that one can make order of magnitude estimates of the H.F. in a given compound by considering the varying covalent character of the metal-ligand neighbor bonds via electronegativity differences.

Like $KFeS_2$, α-$NaFeO_2$[32] and $CuFeO_2$[33] are ternary compounds having iron in high spin trivalent $3d^5$ $^6S_{5/2}$ state and the low temperature magnetic fields (saturation values) observed are 455 ± 5 kOe and 520 ± 5 Koe.

Using the models of Pauling and Hannay & Smyth[9] to measure the re-

lative covalent character of the Fe-S/Fe-O bonds the estimated H.F. for KFeS$_2$ lies in the range from 200 to 244 KOe and is in good agreement with the observed field.

We would like to point out, however, that while making such straightforward comparisons using the values of H.F. for isoelectronic Mn^{2+} & Cr^{+}, in addition to the bonding effects, one must also take into consideration that the core electrons responsible for these fields,are, in the case of Fe^{3+}, in a field of higher Z (atomic number), i.e. are more tightly bound than those corresponding to Mn^{2+} and Cr^{+}.

Finally, we would like to emphasize the fact that the rough estimates obtained throughout this paper using electronegativity differences are well compensated by the realistic insight into the physical differences of the environments provided by such a simple model.

VII. CONCLUSIONS

Summarizing our discussions, we conclude that there appears to be rather extensive evidence that the spread of Mössbauer hyperfine parameters for $^6S_{5/2}$ ions in a variety of host can be attributed mostly to the covalent character of the bonds.

The limited but rather satisfying results discussed in this paper suggest that in the absence of more exact and sophisticated calculations, point charge model, isomer shift calibration (Modified WWJ Plot) and models based on electronegativity differences may be considered as complementary methods for studying charge distributions in complex compounds.

We also suggest that analogous to the Modified WWJ Plot, simple but

readily available models based on electronegativity differences may be usefull for calibrating informative relationships and correlating the spread of hyperfine fields with the covalent character of the bonds.

TABLE I - Electronegativities. (All in Pauling Scale)

Element	Average	Reference
S	2.62	13
Cr	1.50	13
In	1.79	13
O	3.45	13
Fe	1.85	20
Mn	1.5	20

TABLE II - Comparison of the ionic character of iron in $KFeS_2$ determined by various proposed methods

NQ	% Ionic Character	Remarks	References
1	53.3	Point Charge Model	See text
2	53.3	Modified WWJ Plot	7
3	52.0	Ferreira Model	10
4	56.0 - 68.0	**	13 & 14

** Ionic character was determined by extrapolation using the values of ionic character for other sulphides obtained by EPR and NMR.

The models of Pauling and Hannay & Smyth were used to estimate the proportional variations of ionic character.
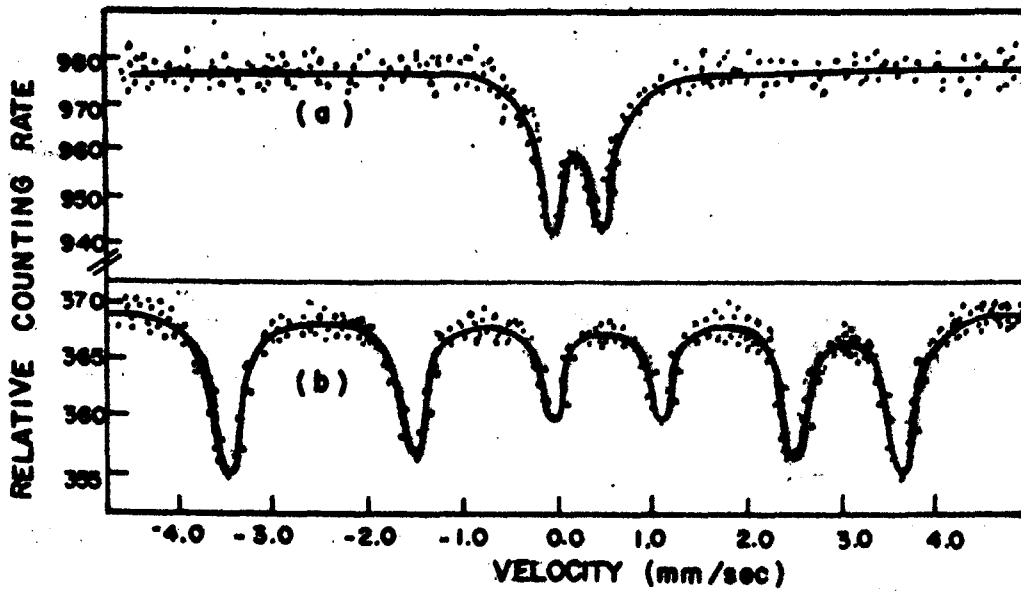
FIG.2 - Mössbauer spectrum of KFeS$_2$ (w.r.t iron):

a) Room temperature and b) Liquid N$_2$ temperature

Ordinate: Transmission (arbitrary units)

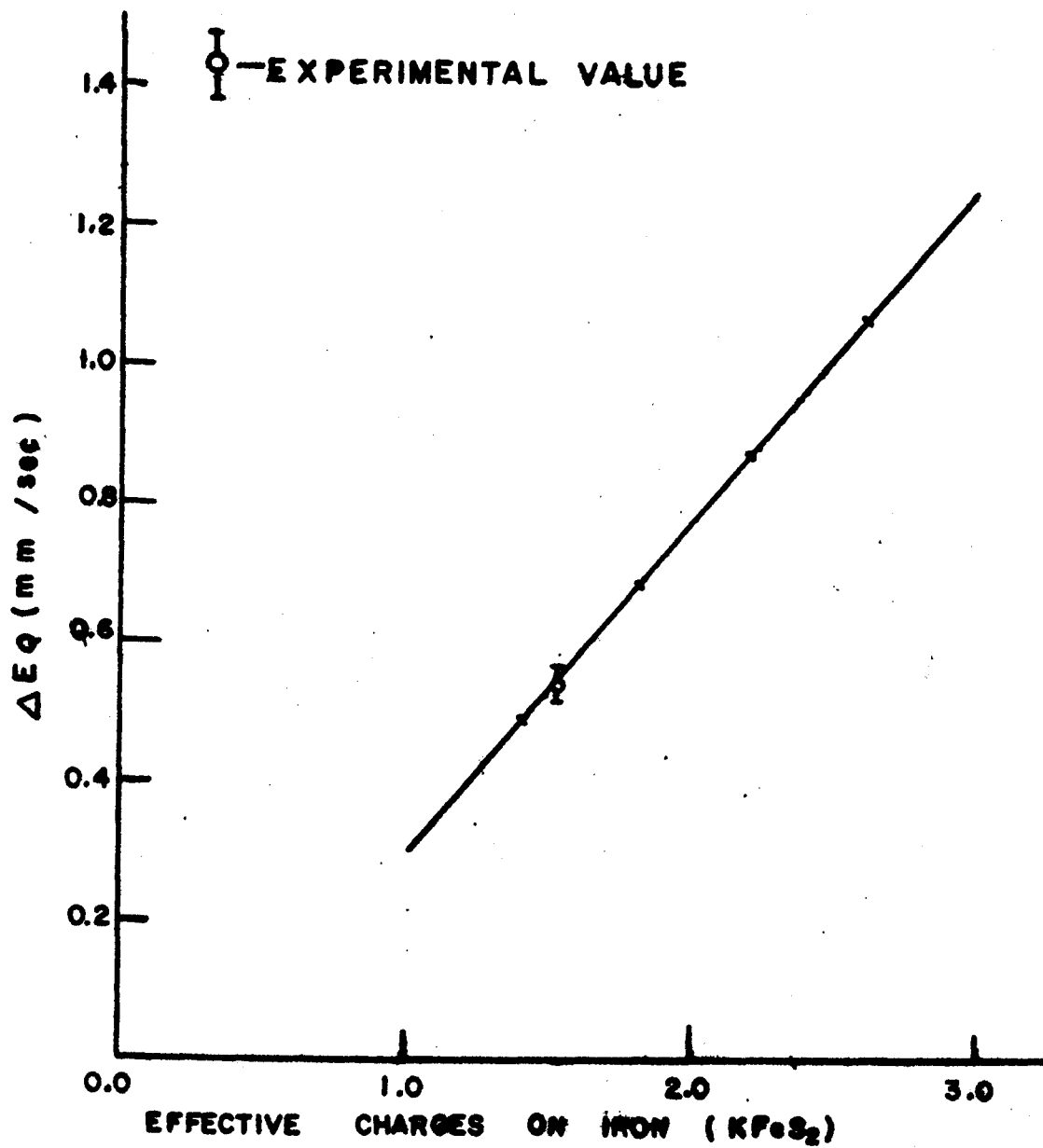Abscissa: Relative velocity of source and absorber (mm/sec).

FIG.3 - Plot of Quadrupole Splitting (mm/sec) from point charge model calculations versus effective charges of iron.

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