THE EFFECTS OF COVALENCY ON THE MOSSBAUER
HYPERFINE INTERACTIONS IN RbFeS$_2$ [+]

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ABSTRACT: Using point charge model calculations, constrained by Mossbauer
              nuclear resonance data, we determine the charge distribution
              and the 4s electron density at the Fe^{57} nucleus in RbFeS$_2$.
              These values are compared with estimates obtained using Danon's
              reinterpretation of the Walker, Wertheim and Jaccarino isomer
              shift calibration (Modified WWJ Plot). The low temperature
              Mossbauer spectroscopic data exhibit the appearance of a mag-
              netic hyperfine interaction at about $-88°$C. The measured hy-
              perfine parameters in this compound are compared with those
              observed for KFeS$_2$ by considering the relative Fe-S covalent
              character, the related x-ray structure parameters and cationic
              radius.

INTRODUCTION

In our previous work[1] we discussed the effects of covalency on the Mossbauer hyperfine interactions in $KFeS_2$ and expressed our interest in extending our work to other compounds of the series of alkali-dithioferrates (III). The structure of $RbFeS_2$ is analogous to that of $KFeS_2$ having iron tetrahedrally bonded to sulphur.

We have emphasized in this paper the use of simple available models for determining the amount of covalency in tetrahedrally bonded iron compounds and the effects of this bonding on the measured hyperfine parameters. The bonding properties in these compunds are reasonably well described by assuming $4sp^3$ hybridization, the participation of $3d$ electrons in the bonding being of less importance. This has been emphasized to be true at least in very covalent crystals and for tetrahedral coordination, where sizable reduction of the hyperfine fields are accompanied by small $3d$ covalency.[2]

STRUCTURE AND EXPERIMENT

$RbFeS_2$ has space-group symmetry C_{2h}^6 with four molecules per unit cell having all Fe atoms at equivalent sites. The $(FeS_2)^-$ ions are arranged in chains of FeS_4 tetrahedra linked by their edges with short Fe-Fe distances. The specimens were prepared from A.R. quality chemicals by fusing iron powder with rubidium carbonate and sulphur and leaching the cold product in water.[3,4] Our samples were characterized by x-ray examination.

Mossbauer spectra of polycrystalline sample were recorded in the standard transmission geometry with a constant acceleration Doppler velocity transducer, 400 multichannel analyzer and Co^{57} in Pd matrix with an activity of 25 mCi. The low temperature measurements were recorded using an Elscint cyrostat with temperature controller. The temperature stability was $\pm 2°C$.

CLACULATIONS OF EFFECTIVE CHARGES AND 4s
ELECTRON DENSITIES

The values of isomer shift and temperature independent quadrupole splitting in $RbFeS_2$ are typical of high spin ferric iron in which the $3d^5$ S-state symmetry of Fe^{3+} does not appear to be significantly affected by covalent

bonding.[2-5] It thus appears reasonable to describe this compound by a simple model of effective charges at all lattice sites which are required to produce the measured field gradient at the Fe nucleus, subject to the additional con-straint imposed by the charge neutrality condition and the monovalent charac-ter of the cations.

Using the available crystallographic data[3,4] the nine components of the *EFG* tensor were calculated from the relation

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

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.[1,6] The *EFG* tensor thus obtained was diagonalized and the principal values of V_{ij} were designated according to the convention that

$$|V_{zz}| > |V_{yy}| > |V_{xx}| \qquad eq = V_{zz}, \qquad \eta = (V_{xx} - V_{yy})/V_{zz}.$$

These values and the latest values[1,6] of Q and γ_∞ are used to calculate ΔE_Q from the relation

$$\Delta E_Q = \tfrac{1}{2} e^2 qQ (1 + \eta^2/3)^{\frac{1}{2}} (1 - \gamma_\infty).$$

The lattice sum calculations were carried out on an IBM 370 computer within a chosen radial distance from the central iron and this radius of summation was systematically varied until the convergence was attained. Variations were also not significant when the uncertainties of the structure were taken into account. All our final results were calculated within a sphere of 50 Å radius.

The electronegativity difference values, and comparison of the sum of ionic radius of Rb and S with the observed bond length, indicates that the al-kali metal in this compound is ionic in character. We therefore assigned charge 1.0 to Rb, a wide range of effective charges to iron and the corresponding charges on sulphur were determined by the charge neutrality condition.

Our calculations yield a best fit with our experimentally determined value of quadrupole splitting (0.45 mm/sec) when we assign charges of ap-proximately 1.46 (units of electron charge) to iron in $RbFeS_2$.

Assuming each of the $4sp^3$ tetrahedral bonds as equivalent, the frac-tional $4s$ electron density at the Fe nucleus in this compound can be deter-mined from

$$4S = (3.0 - E.F.)/4$$

where $E.F.$ is the effective charge on iron previously determined. This estimate yields electron density of 0.38 in $RbFeS_2$.

The total s-electron density at the Fe^{57} nucleus in this compound may be written as the sum of the inner-shell contribution and a fraction $X \psi_{4s}^2(0)$ of $4s$ density arising from the partial occupation of this shell by electrons from the ligands[7,8]

$$\psi_s^2(0) = \sum_1^3 \psi_{is}^2(0) + X\psi_{4s}^2(0).$$

The isomer shift is proportional to the total s electron density $\psi_s^2(0)$. The proportionality constant $a = -0.2 \ a^{-3}$ mm/sec was determined[7,8] from models based on electronegativity differences and molecular orbital calculations and is in agreement with more recent evaluations.[9]

The $4s$ density thus calculated[7,8] for rubidium dithioferrate (III), using the experimental value of isomer shift, is approximately 0.37. This value supports our above estimate.

We would like to note, however, that one should not be carried away by these calculations, since we have used the simplest of theoretical models available and must also make allowances for the uncertainties in our experimental measurements and coupling constants used in these determinations. These calculations do suggest, however, a rather significant iron covalency in $RbFeS_2$, slightly higher than that previously determined for $KFeS_2$.[1] Our calculations[1] indicated 0.35 $4s$ density at the Fe^{57} nucleus in $KFeS_2$. These estimates will also be used to correlate the unusually small values of internal magnetic fields with the covalent character of the bonds.

TABLE I

Experimental Measurements of Hyperfine Parameters

Compound	Isomer Shift[a] (mm/sec)	Quadrupole Splitting[b] (mm/s)	Magnetic Field[c] (kG)
$KFeS_2$	0.37	0.53	215
$RbFeS_2$	0.34	0.45	196

[a] Saturation values (w.r.t. Fe). Experimental errors are ±0.02 mm/sec.

[b] Temperature independent values. Experimental errors are ±0.02 mm/sec.

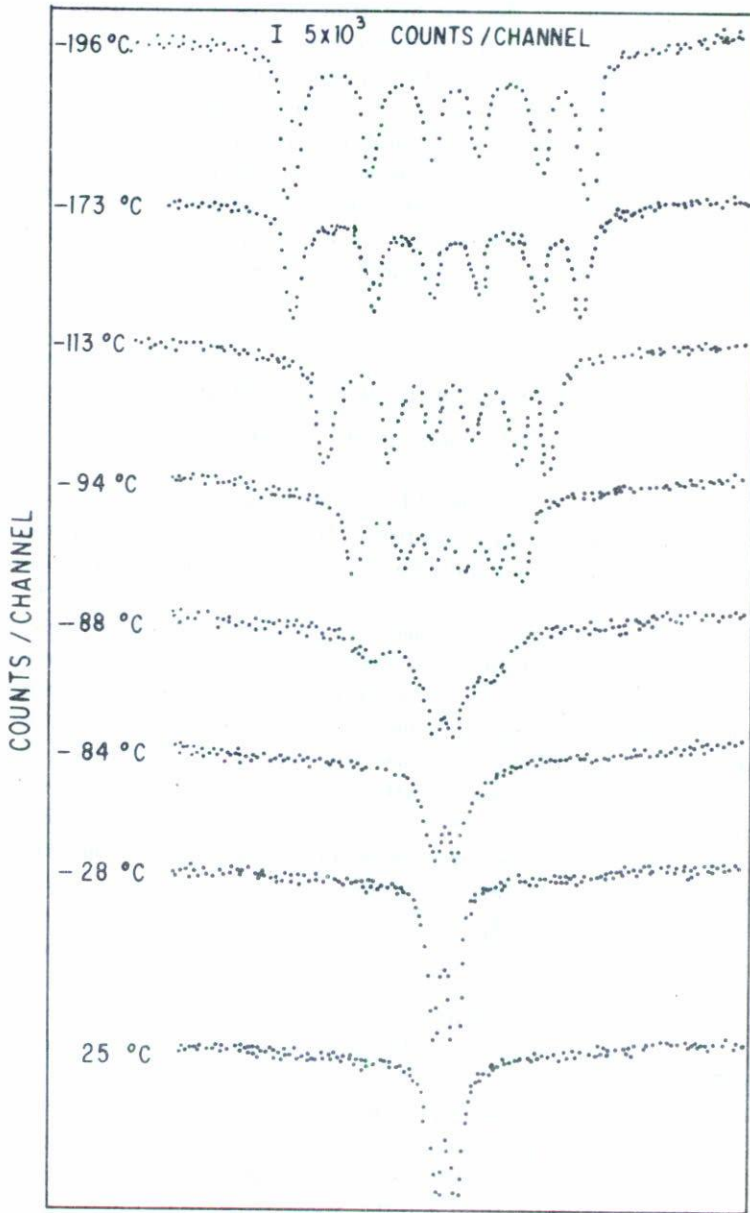[c] Saturation values. Experimental errors are ±5 kG.

Fig. 1. Mossbauer spectrum of RbFeS$_2$ from room temperatures down to liquid nitrogen temperature.

It has been noted[7,8] that the hyperfine parameters are usually larger for more ionic compounds as compared to those which are more covalently bonded. This is in conformity with our experimental measurements (Table I) which indicate that the larger values of hyperfine parameters correspond to the more ionic compound $KFeS_2$. It would thus appear that the larger cations in $RbFeS_2$ tend to force the Fe and S atoms into closer bonds. Such a comparison is at least reasonable for isostructural compounds and would explain the smaller values of hyperfine parameters and the Fe-S distance in $RbFeS_2$ as compared to the analogously structured compound $KFeS_2$.

ANALYSIS OF THE LOW TEMPERATURE MOSSBAUER
SPECTROSCOPIC DATA

The Mossbauer spectra for $RbFeS_2$ from room temperature down to liquid nitrogen temperature (Fig. 1) confirms magnetic ordering at about $-88°$ $\pm 2°C$ and shows a significant increase in isomer shift on passing the transition point.

If the isomer shift (δ) is assumed to be independent of temperature, $(-\partial \delta / \partial T)$ is proportional to the specific heat. The deviation below the transition point may be explained by a temperature dependent component of the isomer shift which is approximately proportional to the magnetic field.

Magnetic susceptibility measurements and crystal structure analysis suggest that Fe is antiferromagnetically coupled in these compounds.[3,4] For interactions between cations in tetrahedral sites correlation superxchange and cation-cation interactions are both unambiguously antiferromagnetic for d^5-d^5 interactions.[9] For Fe-Fe (d^5) interactions, the Anderson's exchange integral[9] is given by $J_{ij} = -2b_{ij}^2/4S^2U$, where $S = 5/2$ and U is the electrostatic energy. The dominant parameter b_{ij} is proportional to the orbital overlap and increases exponentially with decreasing Fe-Fe separation.[9] This would explain the lower transition temprature in $RbFeS_2$ in which the Fe-Fe distances are correspondingly larger than in $KFeS_2$ which has a higher transition temperature ($-28°C$).

Our previous EFG calculation indicated small values of the asymmetry parameter, on the order of 0.09. Consequently, if we neglect direct magnetic and magnetostrictive effects on the quadrupole coupling, the angle between the internal magnetic field and the symmetry axis of the EFG tensor can be determined from the relation

$$3 \cos^2 \theta - 1 = 8 \, \epsilon/e^2 qQ$$

where $e^2 qQ$ can be obtained from the quadrupole splitting and the parameter ϵ can be deduced from the line positions in the Mossbauer spectrum. The estimated value is $18° \pm 5°$.

The measured saturation value for rubidium dithioferrate is 196 kG. The saturation value for the hyperfine field in this compound is unusually small for a ferric ion. These compare however with the values found in some covalent materials and are much smaller than the ionic value of 630 kOe.[10]

Apparently there are considerable covalency effects perhaps also negative contributions from neighboring spins. Zero point motion of the spins cannot account for such a large reduction. It has also been shown that the apparent percentage of delocalization of the antibonding $3d$ electrons in the $^6S_{5/2}$ state to the neighboring atoms is generally very small and cannot be the primary cause for the reduction of the hyperfine fields.

The observed values of hyperfine fields are appreciably larger for ionic crystals than for covalently bonded ones and it has been often emphasized that the magnitude of the internal field in an iron (III) complex is a good indication of the extent of covalency, the more covalent the bonds, the smaller the observed hyperfine fields.[1,2,7-10] This would certainly explain the correspondingly smaller field in $RbFeS_2$ which is more covalently bonded than $KFeS_2$.

It was thus considered of interest to make order of magnitude estimates of these fields in the alkali-dithioferrates using the available covalency models.

Molecular orbital calculations suggest that there should be a linear relationship between the covalent induced hyperfine field and the charge transfer to the 4s state.[2]

Assuming such a relationship, we can write

$$H_{bf} = H^{\text{ionic}} - \triangle H, \; \triangle H = Q_{4s} \times H_{4s}$$

where H^{ionic} is the ionic field and H_{4s} is the average hyperfine field due to unpaired 4s electrons.[10] Q_{4s} is the 4s contribution from the sulphur ligands previously determined.

The estimated hyperfine field is approximately 132 kG which is a reasonable result considering the simplicity of our model. A more proper estimate should take into consideration other contributions, such as the 4s radial polarization which is at present, less accesible.

We have determined from our *EFG* calculations the effective charges

on iron in $KFeS_2$ and $RbFeS_2$ as 1.6 and 1.46 respectively. Using these values of effective charges and assuming the fields are proportional[1,2,7-11] to the ionic character $(E.F./3.0)$ of Fe^{3+}, then the estimated internal field for $RbFeS_2$ is 192 kG in good agreement with the measured value of 196 kG.

We would like to emphasize the fact that these results were obtained by using very simple models and have not by far exhausted all possible contributions. However, we would like to note, that in the absence of more exact and sophisticated calculations, the uncertainties involved in these estimates are well compensated by the realistic insight into the physical differences of the environments provided by such simple models.

ACKNOWLEDGEMENTS

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RESUMEN

Usando cálculos con modelos de cargas puntuales, restringidos por los datos de resonancia nuclear Mossbauer, determinamos la distribución de carga y la densidad de electrones 4s en el núcleo Fe^{57} en el $RbFeS_2$. Estos valores se comparan con estimaciones obtenidas usando la reinterpretación de Danón de la calibración del corrimiento isométrico de Walker, Werteim y Jaccarino (gráfica WWJ modificada). Los datos espectrocópicos Mossbauer a bajas temperaturas exhiben la aparición de una interacción hiperfina magnética cerca de $-88°C$. Los parámetros hiperfinos medidos en este compuesto se comparan con los observados para el $KFeS_2$, considerando el carácter covalente relativo Fe-S, los parámetros de estructura correspondientes obtenidos por rayos X y el radio catiónico.