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MÖSSBAUER STUDIES OF NaFeS₂ : MAGNETIC HYPERFINE FIELDS AND COVALENCY IN MFeS₂ COMPOUNDS (M=Na, K, Rb, Cs) (*)

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Résumé. — L'étude Mössbauer de NaFeS₂, de la température ambiante à celle de l'hélium liquide, révèle la présence d'ordre magnétique en dessous de 77 K. Le champ hyperfin à 4,2 K est de 270 kOe. Les paramètres hyperfins du fer dans NaFeS₂ indiquent la configuration à spin fort de Fe³⁺ (6S⁵/₂). Nous montrons que les valeurs réduites du champ hyperfin dans NaFeS₂ comme dans les composés MFeS₂ (M=K, Rb, Cs) peuvent se corrêler à l'aide de notions simples : champ hyperfin transféré par les électrons 4s, électronegativité des cations.

Abstract. — Mössbauer studies of NaFeS₂ from room temperature down to liquid helium temperature indicate a magnetic ordering below 77 K. The magnitude of the hyperfine field is 270 kOe at 4.2 K. The measured hyperfine parameters characterize iron in NaFeS₂ to be in the high spin Fe³⁺ 6S⁵/₂ configuration. We show that in NaFeS₂ — as in the other MFeS₂ compounds (M=K, Rb, Cs) — the reduced values of hyperfine fields (150-270 kOe) can be correlated with simple concepts such as transferred hyperfine fields via 4s contribution and cationic electronegativity.

1. Introduction. — In our previous work we reported on Mössbauer studies of covalency effects in alcali-dithioferrates AFeS₂ (A=K, Rb, Cs). These effects cause a large reduction of the observed magnetic hyperfine fields from the expected ionic value [1, 2].

In this work I report on Mössbauer studies of NaFeS₂ in the temperature range (300-4.4 K) indicating also a large deviation of the measured magnetic field from the ionic value.

It is interesting to note that the magnitude of the magnetic field in the alcali-dithioferrate series can be correlated with a covalency scale based on 4s contribution and cationic electronegativity.

2. Experimental. — The samples were investigated using a 1024 multichannel analyser, operating in the multiscaler mode to a velocity transducer of the Kankeleit type. The source was a 10 mCi of ⁵⁷Co in a Pd matrix having a width of 0.28 mm/s measured against a natural iron absorber. The gamma rays were detected with a thin NaI (TI) scintillator mounted in a photo-multiplier tube. The liquid helium measurement was taken with both source and absorber in liquid helium. The low temperature measurements were recorded using an Elscint cryostat with temperature controller. The temperature stability was ± 2 °C. The samples were prepared by fusing iron powder with sodium carbonate and sulphur and leaching the cold product in water.

3. Results and discussion. — Figure 1 shows the transmission spectra of NaFeS₂ at several temperatures. From 300 K down to 77 K a quadrupole doublet with a temperature independent splitting of 0.58 mm/s is observed. The room temperature isomer shift value is 0.36 mm/s (w.r.t. Fe). These parameters are typical for iron in the high spin Fe³⁺ ⁶S⁵/₂ configuration [1-4]. At 4.4 K the spectrum was additionally split by a strong magnetic hyperfine interaction and the magnitude of the hyperfine field was |Hₜₕ| = 270 kOe (± 5 kOe). The sign of Hₜₕ is assumed to be negative as this is usually the case in Fe³⁺ high-spin compounds.

Electric field gradient (EFG) calculations [1, 2] in this series of compounds indicated negligible values of asymmetry parameter (η). In the present case of a small quadrupole interaction superimposed on a large magnetic hyperfine interaction in the absorber, the observation of an unchanged quadrupole splitting (¹) indicates that the main axis of the EFG coin-

(*) This paper was presented at the International Conference on the Applications of the Mössbauer Effect, Corfu (Greece) 1976.
Absorption spectra for NaFeS$_2$ at various temperatures.

The magnitude of the internal field in NaFeS$_2$ (270 kOe) which is assumed to be the saturation field, is unusually small for a ferric ion. There are apparently considerable covalency effects from neighboring spins. 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. Assuming such a relationship we can write [1]

$$H_{hf} = H^{\text{ionic}} + \Delta H, \quad \Delta H = Q_{4s} \times H_{4s}$$

where $H^{\text{ionic}} = -630$ kOe is the ionic field and $H_{4s} = +1348$ kG is the average hyperfine field due to one 4s electron and $Q_{4s}$ is the number of 4s electrons at the Fe$^{3+}$ ion originating from the covalent ligands. From the Modified WWJ Plot [1] one obtains $Q_{4s} = 0.22$. This estimate yields $H_{hf} = -330$ kOe, which is a reasonably good estimate.

Various attempts have been made to correlate the extensive Mössbauer data with available electronegativity scales [5]. In this isostructural series MFeS$_2$ (M=Na, K, Rb, Cs) in which the cation M is the only varying element, it appears reasonable to attempt such a correlation. The increasing electronegativity of the cation will decrease the 4s electron density at the Fe nucleus and hence reduce the proposed transferred hyperfine fields. One would thus expect the compounds with the larger electronegativity values to be more ionic, i.e., have larger values of hyperfine fields. The fields measured at 4.4 K are considered as saturation values (for Na and CsFeS$_2$) and as negative. In figure 2, I have plotted the measured values of magnetic field vs cationic electronegativity [6, 7], which suggests that the cationic electronegativity is effectively a good covalency parameter in this series of compounds.

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