On the Mössbauer Effect of Chalcopyrite (*).

F. ARAMU and T. BRESSANI

Istituto di Fisica dell'Università - Cagliari

P. MANCA

Istituto di Fisica dell'Università - Cagliari
Gruppo Nazionale di Struttura della Materia del CNR

(ricevuto il 19 Aprile 1967)

Summary. — We have examined the Mössbauer absorption spectrum of the $^{57}$Fe 14.4 keV $\gamma$-rays from the CuFeS$_2$ compound, at room temperature and liquid-nitrogen temperature. From the experimental values of the isomeric shift we infer that the chalcopyrite may be represented by the resonant configuration Cu$^{+}$Fe$^{3+}$(S$^{-2}$)$_2$ $\leftrightarrow$ Cu$^{-3}$Fe$^{-}(S^{+2})_2$. This configuration may also account for a description of both semiconducting and magnetic properties of the compound.

1. - Introduction.

Chalcopyrite (CuFeS$_2$) type structure, of $D_{4d}^2$ symmetry, (1) is peculiar to a class of semiconducting compounds of general formula ABX$_2$ (2-4), where A, B and X are respectively elements of the I, III and VI group of the periodical table.

An interesting problem in these compounds is a correct knowledge of the interatomic bonds. In this work we are concerned with the examination of CuFeS$_2$ which can be considered as a prototype in this class of materials.


PAULING and BROCKWAY (1) from X-ray experiments concluded that CuFeS₂ is a mixture of the two extreme ionic states \( \text{Cu}^{+}\text{Fe}^{+3}(\text{S}^{-2})_2 \leftrightarrow \text{Cu}^{+2}\text{Fe}^{+2}(\text{S}^{-2})_2 \) and KURILENKO (4) discussed his results of K-absorption spectrum in terms of the existence of two kinds of iron atoms in different lattice sites. The electrical transport properties of CuFeS₂ are typical of a p-type semiconductor with an energy gap of 0.5 eV (5) and a very low mobility.

Neutron diffraction experiments (6) showed that effective magnetic moments of 3.85 and \((0.0 \pm 0.2) \mu_B\) are respectively associated to the iron and copper atoms and that the compound exhibits an antiferromagnetic behaviour with a Néel temperature of 550 °C. TERAISHI (7), from classical magnetic measurements, reported that the value \( S = \frac{3}{2} \) is the most appropriate for the total spin. This result, in the only spin approximation, is consistent with the 3.85\( \mu_B \) value of the effective magnetic moment of iron atoms.

It is difficult, at this point, to interpret this low value of the effective magnetic moment on the basis of the resonant valence state \( \text{Fe}^{+3}e^- \leftrightarrow \text{Fe}^{+2} \) postulated by PAULING and BROCKWAY. This fact has led us to perform an experiment on the Mössbauer resonance absorption of CuFeS₂ to obtain more information on the nature of its interatomic bonds.

2. - Experimental procedure and results.

The Mössbauer absorption measurements were performed with a constant velocity drive analyser of commercial type (*). We used a 2 mC source of \(^{57}\text{Co} \) diffused in a copper matrix, which gives an unsplit line. The source was always kept at room temperature. The γ-ray detector was a proportional counter filled with Kr + N₂ at atmospheric pressure (**).

The absorbers were composed of natural powdered CuFeS₂ from the « Fun-tana Raminosa » mine, Sardinia.

For the room temperature measurements, the powder was uniformly sprayed on a thin cellophane tape. The mean thickness of this layer was equivalent to 2.3 mg cm⁻² of natural iron, as measured by means of the attenuation of the 14.4 keV γ-rays and using the known atomic cross-sections.

For the liquid-nitrogen temperature measurements, the powder was mixed with a small amount of silicon grease and deposited on a 27 mg cm⁻² thick Al-disk

---

(4) Supplied by NSEC, Pittsburg, Pa., mod. B.
(*) Reuter-Stokes RSG-30A.