

## MAGNETIC SUSCEPTIBILITY, TRANSPORT AND MÖSSBAUER MEASUREMENTS IN $\text{CuFeSe}_2$

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The study of the magnetic, transport and Mössbauer properties of eskebornite,  $\text{CuFeSe}_2$ , shows significant differences from that of its homologous sulfide, chalcopyrite ( $\text{CuFeS}_2$ ). From room temperature down to 77 K,  $\text{CuFeSe}_2$  is paramagnetic and metallic with a non-magnetic Mössbauer spectrum showing two equally populated sites for iron with very small quadrupole splitting. It seems clear that the electronic state of iron has evolved in going from chalcopyrite to eskebornite, in which it has a very weak magnetism.

### 1. Introduction

In the way of studying semimagnetic semiconductors (SMSC) of the I-III-VI<sub>2</sub> class we have undertaken the investigation of the magnetic and transport properties of  $\text{CuFeSe}_2$ . The natural mineral with this composition is named eskebornite and was discovered rather recently, in 1949 [1]. This is the analogous selenide of the well studied chalcopyrite ( $\text{CuFeS}_2$ ). Previous works have shown some unexpected differences in the properties between these compounds [2–4]. Contrarily to  $\text{CuFeS}_2$ , magnetically ordered at  $T_N = 823$  K, the Mössbauer spectra of eskebornite are non-magnetic down to 77 K [2]. The structure, not yet unambiguously determined, is presently in a rather puzzling state. In ref. [3] a chalcopyrite-type structure is proposed, while in ref. [4] a sulvanite-type is suggested. Our first results on  $\text{CuFeSe}_2$ , encouraged us to complete an exhaustive work on this compound. Here we present our main initial results on Mössbauer spectroscopy, magnetic susceptibility and transport measurements.

## 2. Experimental

The compound CuFeSe<sub>2</sub> was prepared by the usual melting and annealing technique. A charge of 1.5 g of the desired stoichiometry was sealed under vacuum in a quartz capsule. The components were then melted together at 1150 °C, and the ingot thus obtained was annealed for 30 days at 600 °C and left to cool down to room temperature inside the furnace. X-ray diffraction measurements were carried out with a Guinier camera using a Mo radiation, with Si as internal standard.

The Mössbauer spectra were recorded in a spectrometer mostly home made (driver with its electronic devices, multi channel analyzer built with an SDK-8085 INTEL microprocessor), which runs in the triangular symmetric mode. The source was <sup>57</sup>Co in palladium. The sample was placed in a cryostat and the spectra were taken at different temperatures, from R.T. down to 77 K, with a precision better than 0.5 K. These spectra were least squares fitted by means of a computer program, with dependent lorentzian lines for each subspectrum. The adjusted parameters are the isomer shift (*IS*), *GA* (FWHM), *QS* (quadrupole splitting) and *CH* (hyperfine field).

The susceptibility measurements were made using the force method in a Faraday balance. The sample was held in a liquid nitrogen cryostat between the poles of an electromagnet with the field set at 3 kG.

The electrical conductivity and the Hall mobility in a magnetic field of 10 kG were measured by the van der Pauw method. The samples were small slices of about 0.5 mm thickness cut from the ingot, in which the electrical contacts consisted of four symmetrical copper electroplated spots with indium soldered copper leads. A thermal probe was used to determine the carrier type.

## 3. Results

The X-ray diffraction lines were indexed assuming a tetragonal structure giving cell parameters of:  $a = 5.539 \text{ \AA}$ ,  $c = 11.060 \text{ \AA}$ ,  $c/a = 2.000$ , slightly different from those determined by Johan [4]. It is to be pointed out that some faint lines attributable to magnetite were observed in some of the X-ray powder photographs.

The Mössbauer results are summarized in figs. 1 and 2. The Mössbauer spectrum shown in fig. 1 is, apart the normal evolution of the second order Doppler shift, almost the same for temperatures ranging from L.N.T. to room temperature. The spectrum, clearly paramagnetic, is interpretable as the superposition of two sub spectra, corresponding to two different sites for iron, (if we exclude the solution of three independent lines corresponding to three sites). There are two ways for fitting them: (i) two quadrupolar doublets or (ii) one doublet and a singlet. In the two cases, the ratio of the areas is almost 1 in the

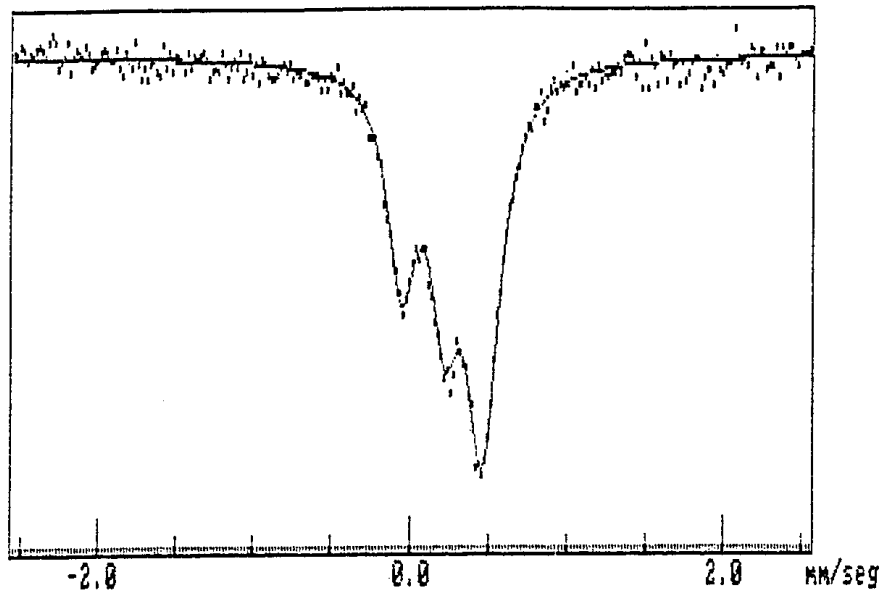


Fig. 1. Mössbauer spectrum of CuFeSe<sub>2</sub> at 77 K.

considered range of temperatures (the FWHM has been fixed to 0.24 mm/s, as the result of the mean value of all the fittings). In fig. 2 the thermal evolution of the Mössbauer parameters (*IS*, *QS*) is reported for case (ii) (very recently, after LACAME90, we obtained new arguments to choose the (ii) solution [7]).

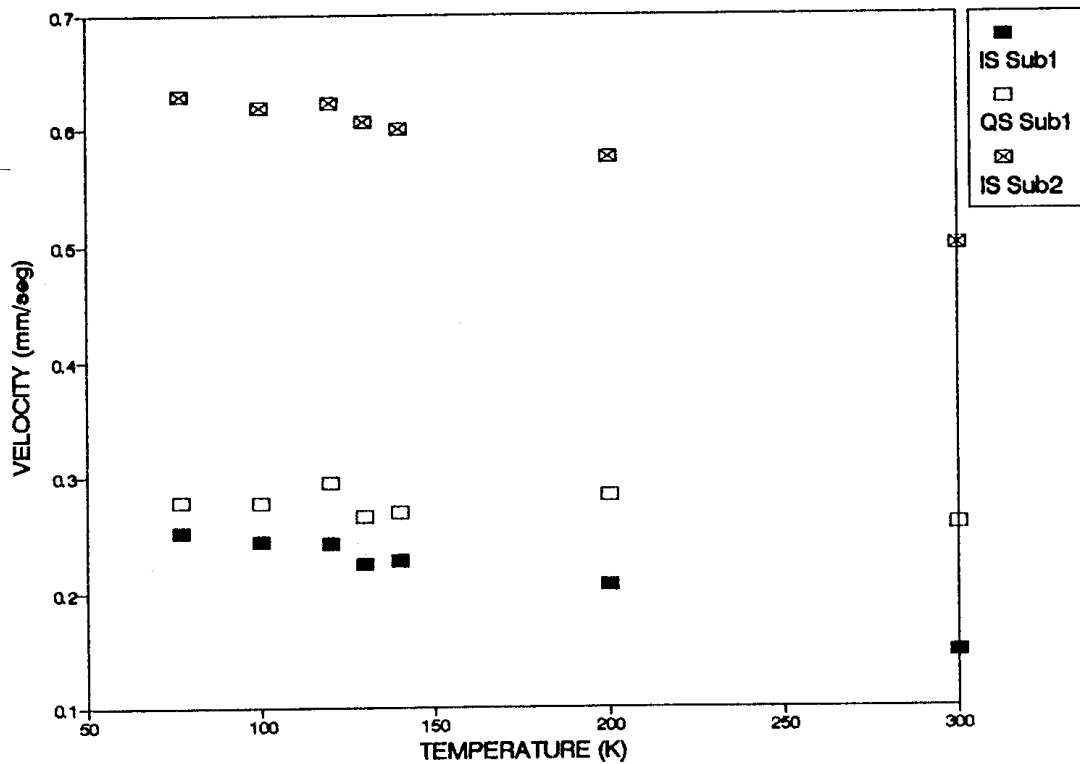


Fig. 2. Thermal evolution of the Mössbauer parameters Isomer Shifts (*IS*) and Quadrupolar Splittings (*QS*).

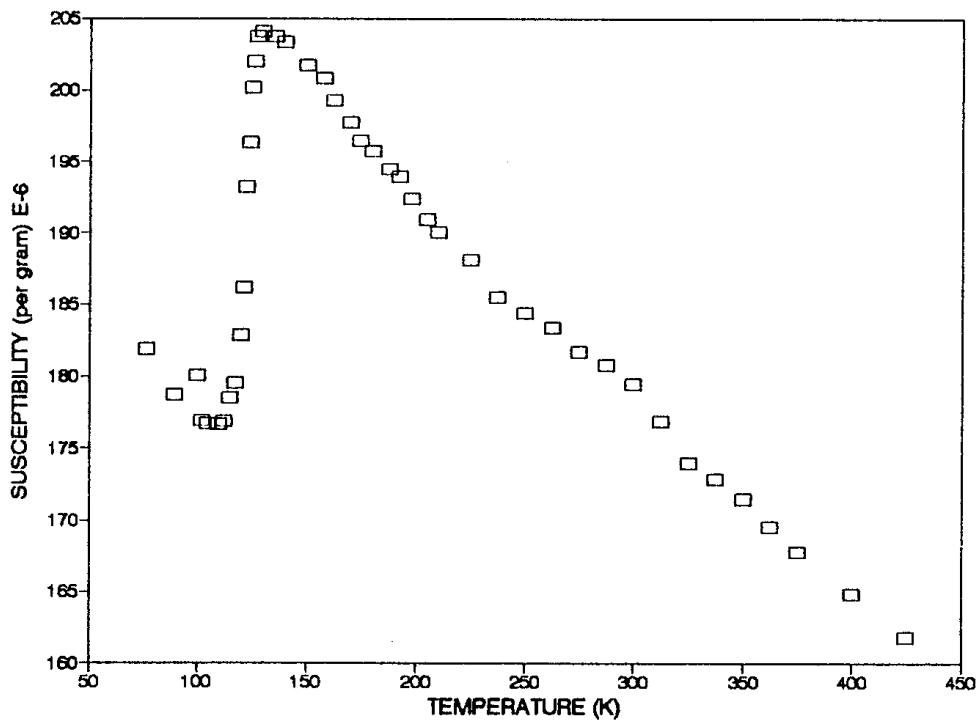


Fig. 3. Magnetic susceptibility of  $\text{CuFeSe}_2$  as a function of the temperature.

The magnetic susceptibility results, which are shown in fig. 3, indicate a Curie-Weiss like behavior down to 130 K, where an abrupt drop is observed below this temperature, indicating a phase transition, whose nature will be commented later. The very high overall value of the susceptibility is an indication of a possible presence of ferromagnetic impurities, in small amounts difficult to detect by Mössbauer spectroscopy.

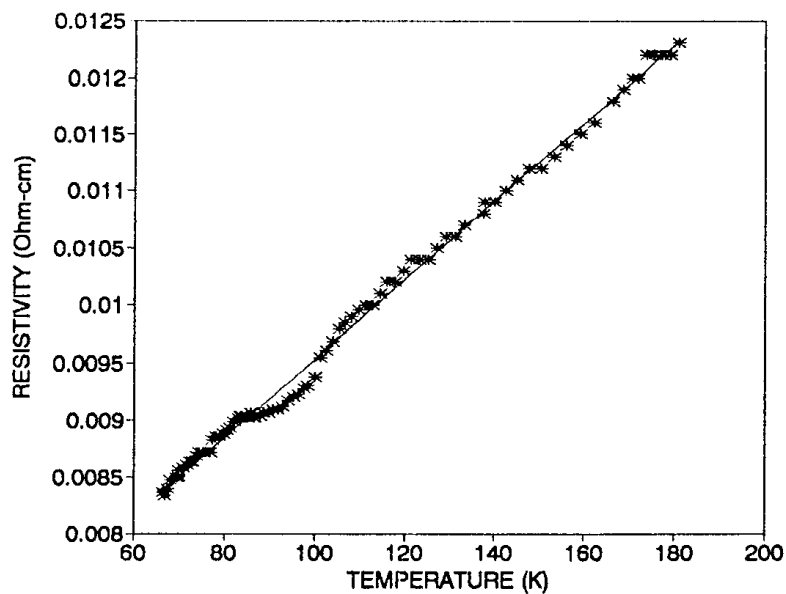


Fig. 4. Electrical resistivity of  $\text{CuFeSe}_2$  as a function of the temperature.

The values of the resistivity as a function of the temperature are shown in fig. 4. The observed linear behavior is characteristic of a metallic conductor. The electrical carriers are of p-type and their concentration is  $10^{22}$  per  $\text{cm}^3$  at 300 K.

#### 4. Conclusions

The susceptibility values are certainly due to the superposition of two contributions, one due to an impurity, certainly magnetite which shows a Verwey transition not very far from  $T = 130$  K, with a very high susceptibility because the  $\text{Fe}_3\text{O}_4$  particles possess a ferromagnetic moment, the other one being the paramagnetic Curie-Weiss like contribution due actually to  $\text{CuFeSe}_2$ .

The relevant properties of eskebornite are that it is metallic with a weak magnetism. These two features are indicative of important changes in the electronic properties of iron and copper in this compound compared to those of chalcopyrite.

Finally, it is interesting to point out that the study of chalcopyrite ( $\text{CuFeS}_2$ ) under hydrostatic pressure at room temperature has shown that:

- 1) at 16 kBars the Mössbauer spectra become non magnetic [5], and
- 2) at 65 kBars it becomes metallic [6].

This behaviour may be compared with that of eskebornite, where one can ask whether the change of sulfur to selenium results in a chemical pressure effect or not.

#### References

- [1] P. Ramdohr, Fortschr. Min. 28 (1949) 69–70.
- [2] K. Viswanatha Reddy and S. Chitra Chetty, Mat. Res. Bull. 11 (1976) 55–70.
- [3] D.C. Harris and E.A. Burke, Canad. Mineral. 10 (1979) 787–796.
- [4] Z. Johan, N.Jb. Mineral, Mh. H.8 (1988) 337–343.
- [5] D.J. Vaughan and J.A. Tossell. Science 179 (1973) 179.
- [6] K. Sato, H. Takahashi, N. Mori and S. Minomura, in: *Proc. Int. Conf. on Ternary and Multinary Compounds*, 15–17 August 1984, eds. B.R. Pamplin, N.V. Joshi and C. Schwab, Prog. in Crystal Growth and Characterization 10 (1985) 125.
- [7] J. Lamazares, F. Gonzalez-Jimenez, E. Jaimes, L. D'Onofrio, R. Iraldi, G. Sanchez-Porras, M. Quintero, J. Gonzalez, J.C. Woolley and G. Lamarche, Int. Conf. on Magnetism - 1991, to be published in J.M.M.M.