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SHORT-RANGE ORDER OF Fe(II) IN SPHALERITE BY MAGNETIC SUSCEPTIBILITY AND ^{57}Fe MÖSSBAUER SPECTROSCOPY

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Several physical properties of sphalerite, which propose cubic ZnS as "tunable" material with non-linear magnetic and magneto-optic properties, are associated to the most common substitutions of Zn by paramagnetic cations (Fe and Mn) thus defining the class of the Diluted Magnetic Semiconductors (DMS). The replacement of Fe and Mn for Zn in sphalerite, where no structural constraints are present, is assumed to occur with a statistical metal distribution. However, the possible presence of short-range ordering phenomena cannot be ruled out, thus affecting the fine electronic properties of this material, which may significantly change as a function of the short-range distribution.

An extensive study of natural and synthetic Fe-bearing sphalerites (Fe-content ranging between 0.005 and 0.250 afu) has been carried out through the combined characterisation of the temperature dependence of the magnetic susceptibility (investigated from 300 to 2 K) and of the room-temperature ^{57}Fe Mössbauer spectroscopic features.

Magnetic susceptibility measurements evidence, in the low temperature range, the presence of clustered Fe(II) even in the most diluted samples, whereas in the high temperature range magnetic data account for the molar contribution in the standard Curie-Weiss model.

All the Mössbauer spectra (may be) are described in terms of variable proportions of three components, namely one singlet and two doublets absorptions, centered at the same isomer shift, relative to isolated Fe(II) ions and different Fe(II) clusters, respectively.

The comparison of all the experimental results points out a self-affinity of Fe(II) ions in sphalerite favoured by the superexchange interaction, which stabilises the formation of clusters even in the relatively diluted samples.