EPR, HF²EPR SPECTROSCOPY AND SQUID STUDY OF NATURAL BORNITE: PRELIMINARY RESULTS

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Bornite (Cu_5FeS_4) is a copper ore mineral of considerable economic relevance, playing an important role in the solar cells, as a composite superconductor, or as a DMS. In order to study its magnetic structure, the metal ions valence distribution and their interactions, X-band and high frequency EPR and magnetisation measurements were performed on a natural bornite sample of the Natural History Museum of Florence University.

The obtained magnetic data show a magnetic phase transition from a paramagnetic to an antiferromagnetic state with a Néel temperature $T_N \sim 75$ K and other discontinuities in the full investigated range (0 - 300 K). The evidence of a further magnetic phase transition was also observable near 30 K.

The experimental Curie constant value found in the high temperature regime is lower than the theoretical value for spin-only Fe(III) ions and suggests a high Fe(II) content. This observation suggest the hypothesis of bornite as a mixed valence system, with electron hopping taking place both between Fe(II) $\leftrightarrow$ Fe(III) and Cu(I) $\leftrightarrow$ Cu(II), the latter being required by charge neutrality. The observed EPR spectra, however, are different both from the typical Cu(II) and Fe(III) spectra. The 300 K and 5 K data show the same very intense peak centred at $g \sim 2.02$, the linewidth of which increases by decreasing temperature. This behaviour is characteristic of a concentrated system, where the exchange interaction prevents the determination of the single ion features. This is in line with a transient redox mechanism between adjacent ions.

Due to the peculiar electronic structure of this semiconductor, paramagnetic resonance experiments have been performed also on powders aged under pressure (1350 atm). The pressed sample, studied at X-band, shows a superposition of two lines, the former at $g \sim 2.02$ and a second, very narrow, at $g \sim 2.00$, thus pointing to an evident pressure influence. In the EPR measurements, performed at 95 and 190 GHz, the narrow line is always observed, whereas the broader X-band EPR line is not detectable.