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MÖSSBAUER SPECTROSCOPY OF Fe-CONTAINING SULFATES

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Mössbauer spectroscopy has been applied to study Fe-containing sulfates of melanterite $M^{2+}[SO_4]\cdot 7H_2O$ ($M^{2+} = Fe^{2+}$, Mn, Co, Zn, Cu), halotrichite $AR_2[SO_4]_4\cdot 22H_2O$ ($A = Fe^{2+}$, Mg, Zn, Mn, Co; R = Al, Fe^{3+}) and copiapite $AFe^{3+}{}_4[SO_4]_6(OH)_2\cdot 20H_2O$ ($A = Fe^{2+}$, Mg, Zn, Cu, Al, Fe^{3+}) groups from the various localities of the Ural, Russia.

Mössbauer spectra of melanterites may be considered as superposition of two doublets corresponding to Fe^{2+} In the spectra of melanterites having compositions most close to ideal $Fe[SO_4]\cdot 7H_2O$, the doublets are characterized by nearly equal isomer shift (δ) and various quadrupole splitting (Δ); squares of both doublets are practically equal that means uniform (1:1) distribution of Fe^{2+} between both sites. Replacement of Fe^{2+} by Cu or/and Zn leads to such effects that ratios of doublet squares are changed from 1:1 to 1:2 and more, indicating irregularity of Fe^{2+} distribution between the structural sites; the values of quadrupole splitting are increased for a site with a smaller part of Fe^{2+} and decreased for a site with a high part of Fe^{2+} The results are in excellent agreement with modern data according to those two types of Fe^{2+} octahedra, M1 and M2, existing in the structure of melanterite. Cu replacing Fe^{2+} is concentrated mainly in the M2 site (PETERSON, 2003).

As distinct from melanterites, sulfates of halotrichite and copiapite groups may contain both Fe^{2+} and Fe^{3+} For this reason, a spectrum is complicated and interpretation is getting more difficult. Mössbauer spectra of halotrichites may be characterized by three doublets at minimum, two of those with the greater values of δ and Δ correspond to Fe^{+2}, the parameters of the doublets being close to that observed for melanterite, giving evidence for the common features in the structures of these minerals (HAWTHORNE et al., 2000). The third doublet, with lower values of δ and Δ is related to Fe^{3+} The spectra of Fe^{2+}-free copiapites from the burnt dumps of coal mines close to ideal alumino- and magnesiocopiapite are characterized by two doublets referring to Fe^{3+} The ratio of doublet squares is 1:1. The spectra of most occurring copiapites containing both Fe^{2+} and Fe^{3+} are supposed as superposition of three doublets, two of those as in a previous case correspond to Fe^{3+} and the third doublet is classified as Fe^{2+}

For halotrichites and copiapites, the contents of Fe total, Fe^{2+} and Fe^{3+} have been defined by methods of wet chemistry. In addition, the contents of Fe^{2+} and Fe^{3+} have been calculated on the base of Fe^{2+}/Fe^{3+} doublet squares and total content of Fe. Differences vary from 0.01 0.43 % for Fe^{2+} and from 0.08 - 0.50 % for Fe^{3+} To calculate the formulae of these sulfates, Mössbauer data give the most satisfactory results.

References

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