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Mössbauer Spectroscopic Study of Danalite, $Fe_4(BeSiO_4)_3S$

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Synopsis. The Mössbauer spectra for danalite have been examined in the temperature range 4.2 to 321 K. The strong temperature dependencies of the Mössbauer parameters are explained on the basis of a ligand field at a tetrahedral site for iron.

The helvite group is a general term of the mineral consisting of $(Mn, Fe, Zn)_4(BeSiO_4)_3S$ in which the cations of the end members are manganese (helvite), iron (danalite), and zinc (genthelvite).[1-3] Metal ions are located in a tetrahedra made of three oxygen atoms and one sulfur atom. An iron(II) ion at a tetrahedral site has been found in spinel-type oxides[4,5] and $MFeCl_4$ type complexes.[6] Their Mössbauer spectra are usually temperature dependent since quadrupole splittings are sensitive to a splitting of the dγ-orbital. There has been no discussion so far regarding the distribution of the splittings of the dγ-orbital, except one paper.[5] In this paper the splitting of the dγ-orbital and its distribution in danalite are examined in terms of Mössbauer spectroscopy.

Experimental

Danalite and helvite occur in the Hirako mine, Hiroshima prefecture[7] and in the Yagisawa mine, Gunma Prefecture,[8] respectively. The apparatus used to carry out the Mössbauer measurements has been reported elsewhere.[9] Every spectrum was fitted to Lorentzian line shapes using a least-squares method at the Computer Center, Kyushu University. The velocity scale was normalized with respect to the center of the spectrum of an iron foil at 297 K.

Results and Discussion

The chemical composition of the danalite used in this study was measured using an X-ray microanalyzer. The distribution of cations was $Fe_{1.94}Mn_{1.58}Zn_{0.39}Ca_{0.09}$.

The Mössbauer spectra for the danalite at three different temperatures are shown in Fig. 1. The value of the quadrupole splitting for the danalite is small (QS=0.369 mm/s) at 321 K, but increases with a decrease in temperature (QS=2.740 mm/s at 4.2 K). The electric field gradient for a high-spin iron(II) ion may be considered as follows.

$$q = (1-R)q_{val} + (1-\gamma)q_{lat}.$$

The subscript "*val*" refers to the charge distribution of an aspherical 3d "valence" electron. The subscript "*lat*" refers to the charge distribution of the neighboring ions in a crystalline lattice. The Sternheimer factors (1-R) and (1-γ) were added to correct for the polarization of an iron(III)-like core. The large temperature dependence of quadrupole splitting of danalite indicates that the splitting of the dγ-orbitals of an iron(II) ion is small and the small quadrupole-splitting values at high temperatures confirm that the contribution of q_{lat} to the electric field gradient is small, although an iron(II) ion is located in an elongated tetrahedral site (one sulfur and three oxygens, "S3O"). From the crystallographic data for helvite, the bond length for Mn–S was found to be 0.2432 nm, and that for Mn–O 0.2082 nm. The bonding angle for S-Mn-O was 116.1 degrees, and that for O-Mn-O was 102.1 degrees.[2] If an electric field gradient $q_{lat}=(Z_i/r_i^3)(3COS^2\theta_i-1)$ is applied for the 1-st nearest "S3O" core with the point charge model, a quadrupole splitting $QS=-1.93$ mm/s can be calculated using the values of Q=0.29 barn and $1-\gamma=-7.17$. The calculated value of q_{lat} is large, due to the elongated tetrahedral structure. Values of q_{lat} are temperature independent on the first approximation and influences the QS value at high temperatures. However, the observed values of QS are smaller at high temperatures than the calculated values. This disagreement may result from the fact that the charge density at a sulfur atom is not the same as that for an oxygen atom and that the contributions to QS from the second nearest neighbor atoms and a further neighbor atoms are important. The splitting of the dγ-orbitals(Δ) may be calculated theoretically.[6]

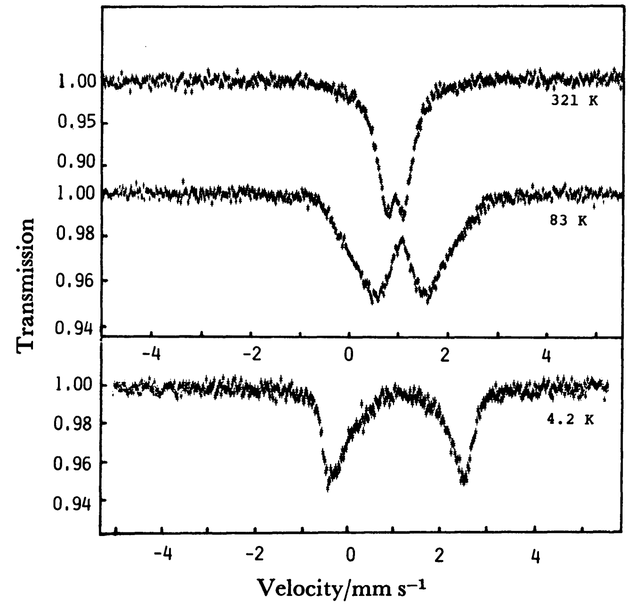

Fig. 1. Mössbauer spectra of the danalite at various temperatures.

$$QS = QS_0 \times \frac{1-\exp(-\Delta/kT)}{1+\exp(-\Delta/kT)},$$

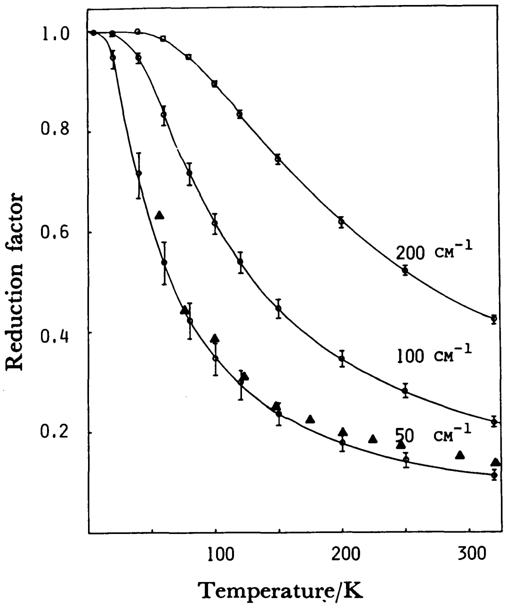

Fig. 2. Temperature dependence of the quadrupole splitting for $\Delta = 50$, 100, 200 cm^{-1} and the experimental values. The bars on the circles show the difference of $\Delta \pm 5$ cm^{-1}. Triangles show the QS values observed for the danalite. The value at 4.2 K is reduced to 1.00.

where k is the Boltzmann constant and QS_0 is taken to be 2.74 mm/s (the value at 4.2 K). Figure 2 shows the plots of the observed values of QS and some theoretical curves. A $\Delta = 50$ cm^{-1} was calculated for the danalite by fitting the theoretical value to experimental measurements. This value seems to be so small for an iron(II) ion located in an elongated tetrahedral site.

The temperature dependence of the full widths at half maximum (FWHM) is plotted in Fig. 3. The differences of QS values between $\Delta = 45$ cm^{-1} and $\Delta = 55$ cm^{-1} at a certain temperature are also plotted as a solid line in the Figure. The difference becomes maximum at a particular temperature. The small geometrical distortion of a tetrahedra brings about the difference of the crystal field strength. This determines the distribution of quadrupole splittings and consequently causes the line width to broaden. The plots of the observed FWHM *vs.* T are similar to the shape of a theoretical curve. A gaussian distribution of Δ with a half width of 5 cm^{-1} explains the observed line broadening, if a gaussian distribution of it is postulated. The observed broad FWHM may come from the nonrandom distribution of cations in danalite.

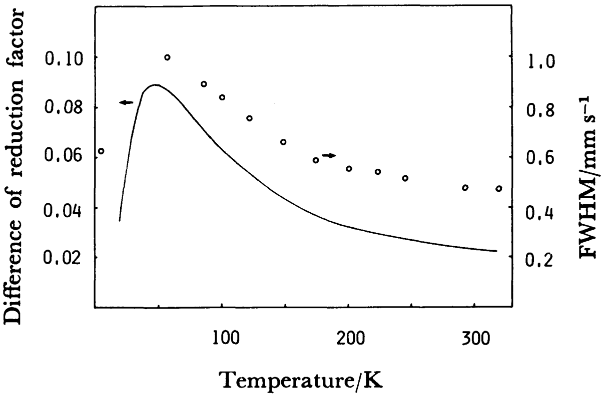

Fig. 3. Temperature dependence of the full width at half maximum for the danalite (open circles) and the differences of the theoretical reduction factors at $\Delta = 50 \pm 5$ cm^{-1} (solid line).

The isomer shifts values are 1.13 (4.2), 1.08 (57), 1.07 (83), 1.06 (100), 1.06 (122), 1.04 (149), 1.03 (175), 1.01 (201), 0.999 (224), 0.986 (246), 0.959 (293), and 0.944 mm/s (at 321 K). The IS values decrease linearly with an increase in temperature and any changes in chemical bonding may not occur in the temperature range from 83 to 321 K. The discovery of the existence of a crystal-field distribution in one compound is due to the existence of a very small splitting of the dγ-orbitals of iron(II) in danalite. Similar QS values and line broadening were also observed for the helvite. This observation supports the idea that a nonrandom distribution of cations brings about such a wide broadening of a spectral line.

References

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