Mössbauer investigations and molecular orbital calculations on epidote

Received: 13 November 2000 / Accepted: 16 May 2001

Abstract The electronic structure of iron-rich epidote has been investigated by cluster molecular orbital calculations in local spin density approximation. Calculated quadrupole splittings for Fe(III) at both the M1 and M3 sites are in quantitative agreement with the experimental values obtained by Mössbauer spectroscopy. A detailed analysis of the theoretical results shows that a strong tetragonal compression of the M3 octahedron is responsible for the unusually large value of the quadrupole splitting of Fe$^{3+}$(III). The corresponding electric field gradient (efg) is dominated by the anisotropy of the valence shell of iron, whereas the ligands contribute only about 15% to the efg. The calculations emphasize that rather large clusters, extending beyond the second coordination sphere of iron, are necessary for a reliable description. Small clusters including only the first coordination sphere of iron generally yield misleading results due to unsaturated oxygen bonds and relatively large cluster charges.

Key words Epidote · Mössbauer spectroscopy · Molecular orbital calculations

Introduction

Members of the epidote group are widespread in low- to medium-grade metamorphic rocks such as calc-silicate rocks, skarns, rodingites, and metabasites. The stability field of epidotes ranges from conditions characteristic of low-pressure hydrothermal systems to significantly higher-pressure environment. Additionally, epidotes may occur as primary phase in calc-alkaline igneous rocks. They consist primarily of the solid solution series between the end members clinozoisite Ca$_2$(Al$_2$Al)Si$_3$O$_{12}$OH and pistacite Ca$_2$[Fe$_2$Fe]$Si_3$O$_{12}$OH. In general, the amount of Fe(III) is restricted to 1.05 Fe per formula unit (pfu). Monoclinic members up to 0.5 Fe pfu are commonly called clinozoisite, and those with more than 0.5 Fe pfu, epidote.

The crystal structure of epidote was first solved by Ito (1950) for an iron-rich species, and subsequently confirmed in detail by various X-ray investigations of other intermediate members of the series clinozoisite-epidote (Belov and Rumanova 1953; Ito et al. 1954; Dollase 1971; Gabe et al. 1973; Carbonin and Molin 1980; Stergiou et al. 1987; Bonazzi and Menchetti 1995), as well as by neutron diffraction (Nozik et al. 1978; Kvicik et al. 1988). All the epidotes studied so far crystallize in the monoclinic space group $P2_1/m$ with two formula units per unit cell, and can be represented by the general formula $A_2M_4Si_3O_{12}$OH. The A sites are occupied by large cations such as Ca, Sr or rare earth elements with high coordination numbers. The three different octahedral M sites generally contain trivalent cations such as Al, Fe(III), Mn(III), etc. Two of the octahedra (M1 and M2) have point symmetry 1 and form chains of edge-sharing octahedra parallel to the crystallographic $b$ axis (cf. Fig. 1). These chains are laterally linked by SiO$_4$ tetrahedra and Si$_2$O$_7$ double tetrahedra to a ring. The octahedral M2 site, as the smallest and most regular site, is occupied exclusively by Al. The M3 octahedra are attached on alternate sides to the chain of the M1 octahedra along its length so that one M3 octahedron shares common edges with two different M1 octahedra. The M3 site has point symmetry $m$ and is the largest and most distorted site (Stergiou et al. 1987). The first Mössbauer study of epidote (Bancroft et al. 1967) showed that Fe(III) preferentially occupies the distorted M3 site. This result was later confirmed by neutron...
The structure of epidote (space group $P2_1/m$)

diffraction measurements (Nozik et al. 1978; Kvick et al. 1988) and other Mössbauer studies (Dollase 1973; Bird et al. 1988; Patrion et al. 1991; Artioli et al. 1995; Fehr and Heuss-Assichler 1997). Fe(III) on the M1 site has not been detected in epidotes with iron content below about 0.75 Fe pfu (Dollase 1973; Fehr and Heuss-Assichler 1997), but in iron-rich epidotes, small amounts of Fe(III) may enter into the M1 position, where the intracrystalline exchange $\text{Al} \Rightarrow \text{Fe(III)}$ between the M1 and M3 sites may be described by a nonconvergent ordering process (Bird and Helgeson 1980). Finally, Mössbauer spectroscopy, as well as magnetic susceptibility measurements, indicate that Fe(III) is in a high-spin electronic state (Burns and Strens 1967).

The Mössbauer spectra of epidotes (cf. Fig. 2) exhibit two peaks of equal intensity. In addition, iron-rich samples with more than 0.75 Fe pfu may exhibit an inner shoulder, indicating the existence of a second doublet. While the isomer shifts $\delta$ of both doublets with values of 0.36 mm s$^{-1}$ are similar and characteristic of Fe(III), their quadrupole splittings $\Delta_\text{Q}$ are distinctly different. All Mössbauer spectra yield values between 1.89 and 2.06 mm s$^{-1}$ (sign has not been determined) for the dominant doublet that has uniformly been assigned to Fe(III) in the more distorted M3 site (Bancroft et al. 1967; Dollase 1973; Bird et al. 1988; Patrion et al. 1991; Artioli et al. 1995; Fehr and Heuss-Assichler 1997). Such a quadrupole splitting is unusually large for high-spin ferrous iron in approximately octahedral coordination. On the other hand, the experimentally determined values for the quadrupole splitting of the less intense doublet in iron-rich epidotes, that is attributed to Fe(III) in the more regular M1 site, varies considerably between 1.33 mm s$^{-1}$ (Dollase 1971), 0.80–1.00 mm s$^{-1}$ (Patrion et al. 1991), 0.97 mm s$^{-1}$ (Artioli et al. 1995), and 1.50–1.62 mm s$^{-1}$ (Fehr and Heuss-Assichler 1997). Although this variation may be caused by structural differences, it seems more likely to be due to uncertainties in evaluating the measured spectra because of the low Fe occupation of the M1 site.