TEMPERATURE DEPENDENCE OF THE Fe²⁺ MÖSSBAUER PARAMETERS IN TRIPHYLITE (LiFePO₄)

Van Alboom, A.[1], De Grave, E.[2] & Wohlfahrt-Mehrens, M.[3]

[1] Department of Industrial Sciences BME-CTL, Highschool Ghent,
Schoonmeersstraat 52, B-9000, Gent, Belgium
[2] Department of Subatomic and Radiation Physics, University of Ghent,
Proeftuinstraat 86, B-9000, Gent, Belgium
[3] Center for Solar Energy and Hydrogen Research, Baden-Württemberg Division 3,
Helmholtzstraße 8, D89081, Ulm, Germany
e-mail: toon.vanalboom@hogent.be

Triphylite (LiFePO₄) has an olivine type structure (Pnma) and has received much attention because of its application as possible electrode active material for lithium rechargeable batteries.

In this work, the temperature dependence of the Mössbauer parameters of Fe²⁺ in synthetic triphylite (ARNOLD et al., 2003) is determined between 4 K and room temperature. From the Mössbauer measurements a sharp magnetic ordening transition is observed at 53 K, which is in line with the Néel temperature as is determined by neutron diffraction (ROUSSE, 2003). The Mössbauer spectra in the paramagnetic region are well fitted by one Fe²⁺ quadrupole doublet with small linewidth. The spectra in the magnetic region are typical for Fe²⁺, showing the maximum of eight absorption lines. They are analysed using the diagonalization of the full nuclear-interaction Hamiltonian and could be successfully fitted with a model independent distribution of hyperfine fields.

The hyperfine field is always collinear to the local principal axis of the electric field gradient tensor. The asymmetry parameter is about 0.79 and the quadrupole coupling constant is 2.79 mm/s, which is perfect in line with the quadrupole splitting $\Delta E_Q = 3.06$ mm/s at 80 K in the paramagnetic region.

The temperature dependence of the quadrupole splitting is interpreted within the ⁵D orbital energy level scheme of Fe²⁺ by a crystal field calculation (VAN ALBOOM et al., 1993) based on the point symmetry of the Fe²⁺ site in triphylite (ANDERSON et al., 2000).

When triphylite is used as electrode material in lithium rechargeable batteries, there is a conversion of triphylite in its delithiated form FePO₄ (heterosite) and vice versa during the charge/discharge process. The characteristic Mössbauer temperature is an important parameter in order to determine accurate ratios of both compounds during the process (ANDERSON et al., 2000). From the temperature dependence of the isomer shift its value is determined to 390 K for Fe²⁺ in triphylite. The intrinsic isomershift is 1.45 mm/s.

References
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