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Temperature dependence of the Fe^{2+} Mössbauer parameters in triphylite ($LiFePO_4$)

Antoine Van Alboom,[1,2,*] Eddy De Grave,[2] and Margret Wohlfahrt-Mehrens[3]

[1]Faculty of Applied Engineering Sciences, University College Gent, Schoonmeersstraat 52, B-9000 Gent, Belgium
[2]Department of Physics and Astronomy, 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

Abstract

The ferrous Mössbauer parameters are determined for synthetic triphylite ($LiFePO_4$) over a wide temperature range between 8 and 900 K. A sharp magnetic order-disorder transition is observed at (52.5 ± 0.5) K. In the paramagnetic state, the Mössbauer spectra are adequately analyzed by one Fe^{2+} quadrupole doublet with a narrow line width of 0.285 mm/s at room temperature. In the magnetic state, the spectra show up to eight absorption lines, which is typical for Fe^{2+}. These spectra are analyzed through diagonalization of the full nuclear-interaction hamiltonian. The hyperfine field B_{hf} is found to be collinear to the local principal axis of the electric field gradient (EFG) tensor. The saturation value for B_{hf} is 125.5 kOe. For temperatures below 52 K, the adjusted value for the asymmetry parameter of the EFG is $\eta \approx 0.8$ and for the quadrupole splitting $\Delta E_Q = 3.06$ mm/s. This latter value is perfectly in line with the value at 80 K (paramagnetic regime). The temperature dependence of the quadrupole splitting is interpreted within the ^5D orbital energy level scheme of Fe^{2+} by a crystal field calculation based on the point symmetry of the Fe^{2+} site in triphylite. The variation of the hyperfine field with temperature is interpreted within the molecular field approximation, however, taking exchange magnetostriction into account. From the temperature dependence of the isomer shift the characteristic Mössbauer temperature Θ_M is determined to be 418 K and the intrinsic isomer shift $\delta_I = 1.46$ mm/s. From these, the Mössbauer fraction at room temperature is calculated to be 0.785.

Keywords: Triphylite, Mössbauer, isomer shift, quadrupole interaction, hyperfine field, liquid helium, crystal field calculation