Electric field gradient tensors at the aluminum sites in the Al$_2$SiO$_5$ polymorphs from CCD high-resolution X-ray diffraction data: Comparison with $^{27}$Al NMR results

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ABSTRACT

High-resolution single-crystal X-ray diffraction intensities recorded with a charge-coupled device detector at low temperature (100 K) were used to derive the electron density distribution in three Al$_2$SiO$_5$ polymorphs: andalusite, sillimanite, and kyanite. The $^{27}$Al nuclear quadrupole coupling tensors were estimated from both the internal polarization contribution of the Al electron density and that of the lattice with electronic multipoles up to octupoles for oxygen atoms and hexadecapoles for Si and Al. Based on new estimations of the $^{27}$Al Sternheimer shielding factor, $R$ and the antishielding factor, $\gamma$, a close agreement was achieved between the quadrupole coupling tensors at the various Al-sites derived from the X-ray diffraction data for all three polymorphs of Al$_2$SiO$_5$ with those determined previously from single-crystal $^{27}$Al NMR spectra.

INTRODUCTION

An important goal of research in mineral physics is the understanding of the physical and thermodynamic properties of minerals at the atomistic basis. A detailed knowledge of the nature of chemical bonding in these minerals is fundamental to these objectives. The three polymorphs of Al$_2$SiO$_5$: andalusite, sillimanite, and kyanite. The $^{27}$Al nuclear quadrupole coupling tensors were estimated from both the internal polarization contribution of the Al electron density and that of the lattice with electronic multipoles up to octupoles for oxygen atoms and hexadecapoles for Si and Al. Based on new estimations of the $^{27}$Al Sternheimer shielding factor, $R$ and the antishielding factor, $\gamma$, a close agreement was achieved between the quadrupole coupling tensors at the various Al-sites derived from the X-ray diffraction data for all three polymorphs of Al$_2$SiO$_5$ with those determined previously from single-crystal $^{27}$Al NMR spectra.

interaction of the quadrupole moment with the charge gradient at the nuclear site, can be very accurately measured by nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) techniques. Because the electric quadrupole moments of the nuclei are well known, the EFG components at the nuclear sites may be easily derived from NMR and NQR measurements and compared with those calculated from the electron density distribution determined either experimentally by single-crystal X-ray diffraction or theoretically by ab-initio quantum mechanical calculations. $^{27}$Al with a 100% natural abundance and a nuclear spin, $I = 5/2$ is a good candidate for NMR studies and consequently, the quadrupole coupling tensors at the Al-sites in a large number of Al-bearing oxides and silicates have been reported (Ghose and Tsang 1973). Because the quadrupole coupling tensors at the Al-sites in aluminosilicates can be measured very accurately by single-crystal $^{27}$Al NMR experiments, they serve as very stringent tests of the accuracy of the electron density distributions, determined either experimentally by X-ray diffraction or theoretically by ab-initio quantum mechanical calculations. Only when such stringent criteria are satisfied, one can with confidence derive physically meaningful conclusions about the detailed differences in the chemical bonding in these minerals using the bond critical properties (Bader 1990; see also Coppens 1997). Although numerous studies of electron densities and properties derived therefrom in a variety of chemical compounds exist in the literature (Coppens 1997), not many comparisons of the EFG components derived from NMR and X-ray measurements on minerals are known. From single crystal $^{27}$Al NMR spectra, the electric quadrupole coupling tensors at the different Al-sites have been measured in andalusite (Hafner et al. 1970; Bryant et al. 1999), sillimanite (Raymond and Hafner 1970) and kyanite (Hafner and Raymond 1967) and by MAS NMR in all three polymorphs (Alemany et al. 1991). Recently, the EFG tensors at the different Al-sites

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