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Ordering of the Al cation distribution in the octahedral sheets related to the ordering of Al in the tetrahedral sheets of phlogopite studied by $\{^1\text{H}\}^{29}\text{Si}$ CPMAS NMR spectroscopy

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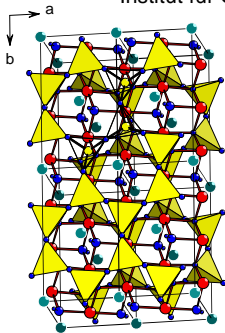


Figure 2. Crystal structure of phlogopite, view on the tetrahedral layers (after Tateyama et al., 1974).

Crystal structure of phlogopite

Phlogopite is a 2:1 layer silicate in which every fourth Si-atom in the tetrahedral layer is replaced by Al, so that an interlayer of K^+ -atoms is necessary for charge balancing (Fig. 1). In pure phlogopite, all three cation sites in the octahedral layer are occupied by Mg. Two of these sites are cis-coordinated by four O-atoms and two OH-groups, while the third one is trans-coordinated (Fig. 2).

In natural phlogopite OH is replaced by F to some extent. Additionally, the substitution $\text{Mg}^{\text{VI}}\text{Si}^{\text{IV}} \leftrightarrow \text{Al}^{\text{VI}}\text{Al}^{\text{IV}}$ (Tschermak's substitution) occurs, concerning both the octahedral and the tetrahedral sheets. CPMAS NMR spectroscopy may shed light onto the degree of ordering of cations in the two types of sheets and answer the question, whether the ordering of cations in the octahedral sheet is related to that in the tetrahedral sheets.

For the experiments synthetic phlogopites with nominal gel compositions

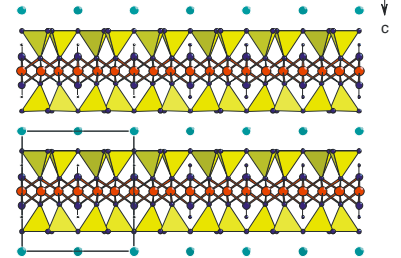
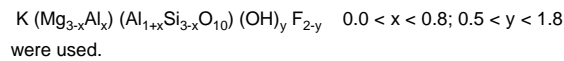


Figure 1. View on the stacking sequence of tetrahedral and octahedral sheets in the crystal structure of phlogopite (after Tateyama et al., 1974).

Cross polarisation (CP) NMR spectroscopy

CPMAS NMR spectroscopy is a useful tool to gather information on interatomic distances and next-nearest-neighbour-relationships, complementary to X-ray diffraction studies. Furthermore, as it is a double resonance experiment (see pulse scheme in Figure 3a), it allows a transfer of magnetisation from a nucleus with a strong magnetic polarisation, such as ^1H , to a nucleus with a low magnetogyric ratio, such as ^{29}Si , to increase the spectral resolution. During the contact time the distance between the energy levels in both the ^1H and the ^{29}Si system becomes equal, which allows an energy transfer from one system to the other (Hartmann-Hahn-condition, Figure 3b).

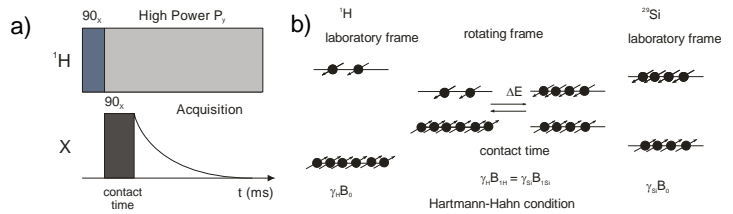


Figure 3. a) Pulse scheme for CPMAS NMR spectroscopy b) Schematic energy level diagram for the two systems ^1H and ^{29}Si before the two pulses (left and right, respectively) and during the contact time (middle).

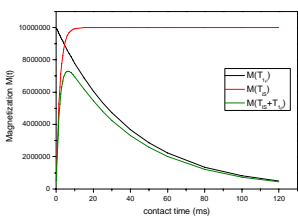


Figure 4. Magnetisation of the ^{29}Si -nucleus as a function of the contact time for a large number of proton spins.

Magnetisation functions

The increase of magnetisation is a function of the contact time t , but also of the number of proton spins and the distance between these spins and the ^{29}Si nuclei. For a large number of proton spins, the magnetisation as a function of contact time is the sum of two effects (Fig. 4, green curve). As soon as the two systems, ^1H and ^{29}Si , are in contact, the magnetisation of the ^{29}Si nucleus increases rapidly to its maximum and then stays constant (red curve, $M(T_{1s})$). Meanwhile, magnetisation decreases because of the spin-lattice-relaxation (black curve, $M(T_{1p})$). The experimentally derived functions of our phlogopite samples (Fig. 5) differ from the theoretical curve inasmuch as they show the sharp increase of magnetisation at short contact times, but hardly any decrease. Therefore, the phlogopites show very low spin-lattice-relaxation, which means that there are only few processes of low frequencies in the lattice.

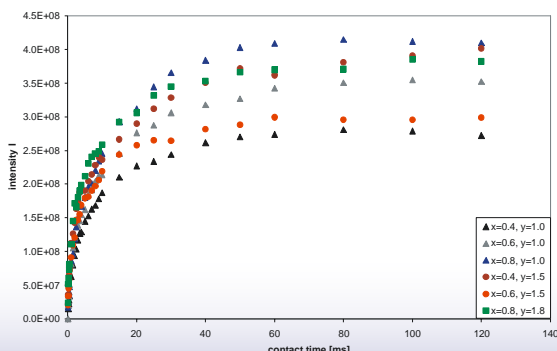


Figure 5. Experimentally derived magnetisation curves for phlogopites of different compositions. From least-squares-fits of the curves, we got values for T_{1s} of 6-8 ms, while T_{1p} is very long or even infinite.

References:

1) Tateyama, H., Shimoda, S., Sudo, T. (1974). Zeitschrift für Kristallographie, Kristallgeometrie, Kristallphysik, Kristallographie, 139, 196-206.

2D CPMAS NMR spectroscopy

If the pulse scheme shown in Figure 6 is used, information on the ^1H environment can be obtained, coupled to that of the ^{29}Si -nucleus. In Figure 7, two examples of 2D CPMAS NMR spectra are shown, for the compositions $x=0.4, y=1.0$ (a) and $x=0.8, y=1.0$ (b).

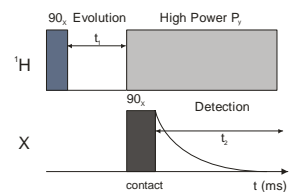


Figure 6. Pulse scheme of the 2D CPMAS NMR experiment.

The two spectra indicate, that OH-groups in the octahedral layer, which are coordinated by three Mg, favour the environment of Si-atoms, which have only one Al-atom as next-nearest-neighbour, in the tetrahedral layer. OH-groups, which are coordinated two Mg and one Al, can be found near Si-atoms with two Al-atoms as next-nearest-neighbours. Hence, we can conclude, that Al-atoms in the octahedral sheet are located near Al-rich environments in the tetrahedral sheet, and that there is a relationship between the ordering in both sheets.

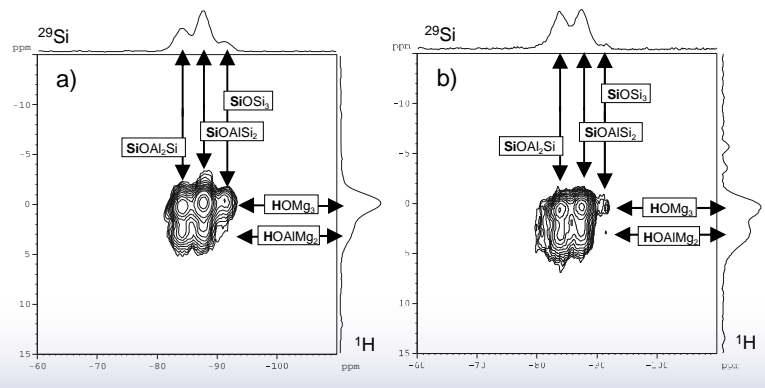


Figure 7. 2D CPMAS NMR spectra of phlogopites of the compositions $x = 0.4, y = 1.0$ (a) and $x = 0.8, y = 1.0$ (b).