Solid-state NMR studies of chemical shifts and quadrupolar interactions in alkali halide solid solutions

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Previously we reported on 21.1 T NMR studies of the quadrupolar nuclei in alkali halide solid solutions which have the NaCl lattice structure, making observations of the effects of the different configurations of neighbouring ions on the observe nucleus. Recent work has focused on solid solutions with the CsCl structure, and on the effects of second ion shell configurations on the spectra of the observed nucleus. The work on CsCl structure types is of narrower scope because fewer compositional combinations exist as solid solutions, e.g. solid solutions of CsBr/CsCl only span the Br-rich half of the composition range, and in the CsBr/RbBr system CsCl-type solid solutions exist for CsBr > ~75% and NaCl-type solid solutions occur for RbBr > ~ 85%.

^{133}Cs NMR spectra for CsBr/CsCl (Figure 1, left) are dominated by chemical shielding, even more so than for ^{87}Rb in the NaCl-type RbBr/RbCl. In 50/50 CsBr/CsCl nine resonances are resolved corresponding to $CsBr_xCl_{8-x}$ species, since in the body-centred cubic lattice (CsCl-type) there are 8

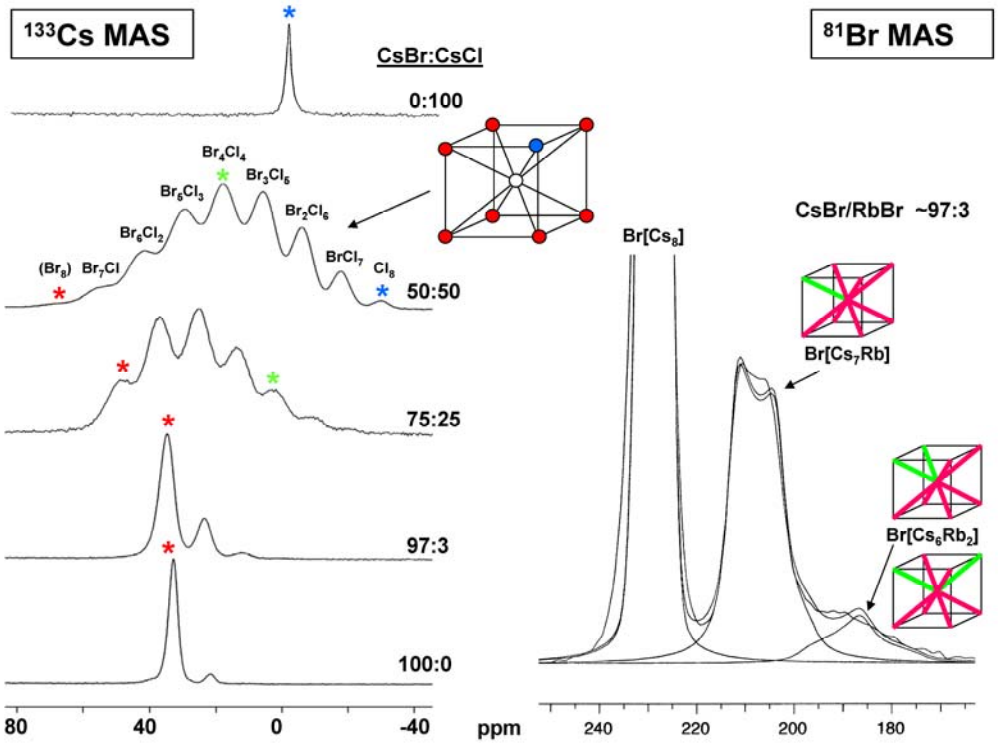

Figure 1: First ion shell effects in body-centred-cubic CsCl-type structures. **Left:** ^{133}Cs NMR spectra (21.1 T, MAS 30 kHz) of solid solutions of CsBr/CsCl. The 50:50 solid solution clearly shows nine resolved peaks corresponding to the different combinations of Br and Cl in the first shell of eight ions. **Right:** ^{81}Br NMR spectrum (21.1 T, MAS 30 kHz) of CsBr/RbBr ~97:3, showing 2nd order quadrupolar lineshapes with $\eta = 0$, C_Q = 4.19 MHz (from fitting) for $Br[Cs_7Rb]$ and $\eta = 1$, C_Q = 4.49 MHz (simulated) for $Br[Cs_6Rb_2]$.

ions in the first shell (as compared to 6 for NaCl-type lattices for which 7 lines are seen). There is a correlation between increasing shift and decreasing lattice dimension, the same as was observed for NaCl-types. The spectra for ^{133}Cs at 21.1 T have slightly better resolution than at 7.03 T in contrast with the drastic improvement in resolution observed at the higher field for ^{81}Br. This emphasizes that ^{133}Cs spectra are dominated by chemical shielding, which benefits from greater shift dispersion at higher field, and 2nd order quadrupolar effects for ^{133}Cs are negligible even at lower fields.

The ^{81}Br spectrum of 97:3 CsBr/RbBr (Figure 1, right) shows chemical shift resolution of the different first shell species, and 2nd order quadrupolar lineshapes for Br[Cs_7Rb] and Br[Cs_6Rb_2] species which are in agreement with the predictions of a simple model for additive contributions to the electric field gradient tensor.

Spectra for ^{133}Cs in CsBr/RbBr and CsI/RbI solid solutions and for ^{35}Cl in CsBr/CsCl show resolved resonances for distinct second shell configurations of ions (Figure 2). For the ^{35}Cl spectrum this is helped by removal of 2nd order quadrupolar effects at the high field. The distance to the second shell ions is significantly smaller in the CsCl-type structure than in the NaCl-type structure (1.1547 times the distance to the first shell ions in CsCl-type versus 1.4142 for NaCl-type). This shorter distance and hence stronger interactions may help explain why the chemical shifts for the different second shell configurations are better resolved in the CsCl-type.

Another interesting second shell effect is that the chemical shifts of the different species increase as the number of smaller ions in the shell increases. This is opposite to what is observed when there are mixed ions in the first shell. This may be connected with the change from attractive interaction between the central ion and the first shell, to repulsive interaction for the second shell.

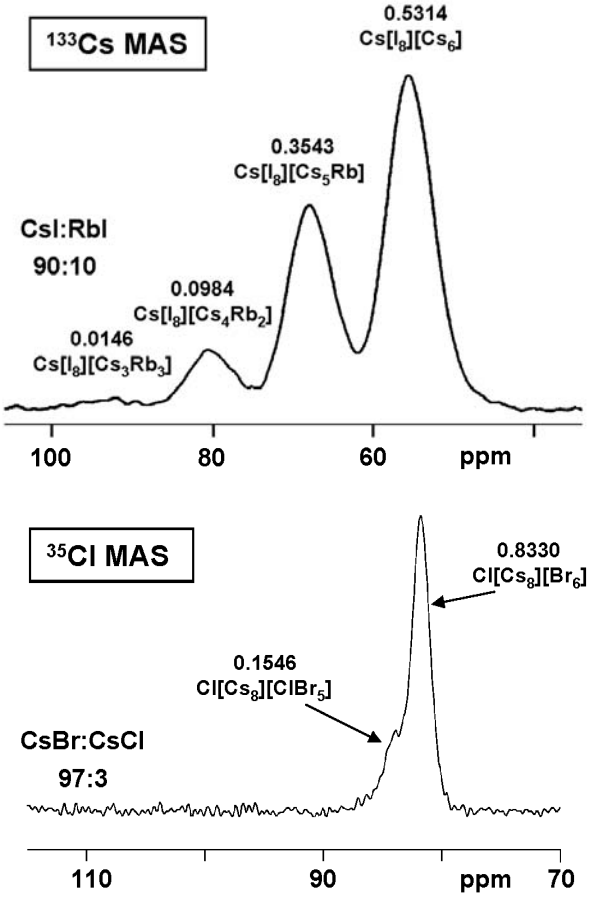

Figure 2: Second ion shell effects in body-centred-cubic CsCl-type structures. **Top:** ^{133}Cs NMR spectrum (21.1T, MAS 30 kHz) of CsI/RbI 90:10, showing resolved peaks corresponding to different combinations of Cs and Rb in the second shell of six ions. The statistical weights of the different species calculated for a 9Cs:1Rb ratio are given above the assignments. **Bottom:** ^{35}Cl NMR spectrum (21.1T, MAS 30 kHz) of a 97:3 solid solution of CsBr/CsCl showing partial resolution of resonances due to different combinations of Br and Cl in the second shell of six ions. Assignments and statistical weights are indicated.