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Spinning-Rate-Dependent Shift in Magic-Angle-Sample-Spinning NMR Observed in Cuprous Halides

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We have found that the isotropic peak position changes depending on the spinning rate of the sample in ^{63}Cu, ^{65}Cu, ^{127}I, and ^{79}Br magic-angle-sample-spinning (MAS) NMR of cuprous halides, CuI, CuBr, and CuCl. The mechanisms which cause the spinning-rate-dependent shift are briefly discussed.

Magic-angle sample spinning (MAS) is a very useful technique to reduce the NMR linewidth characteristic in solids.[1,2] Thereby a number of works have been published,[3] in which chemical shifts in solids have been discussed in a similar way to liquid state. It is generally believed in the MAS NMR experiment the isotropic peak does not change its position even if the spinning rate of the sample is varied. Using this property, we can distinguish the isotropic peak from the spinning sidebands which change their position depending on the spinning rate.

In the course of our work on ^{63}Cu and ^{65}Cu MAS NMR of cuprous halides, we have observed that the peak position is dependent on the spinning rate of the sample. The magnitude of the dependence increases in the following order; CuCl CuBr CuI. Similar dependences have been observed in NMR of halogen nuclei of cuprous halides. To our knowledge, this is the first observation of the spinning-rate-dependent shift in MAS NMR. In this letter, we report the spinning-rate-dependent shift, especially in ^{63}Cu and ^{127}I NMR of CuI.

Cuprous halides were purchased from Nacarai Tesque, Inc. (Kyoto) and Soekawa Chemicals Co., Ltd.(Tokyo), and were used without any purification. NMR spectra were measured by a Bruker MSL400 pulsed spectrometer at room temperature and at the field strength of 9.40 T. The shift values are given with the higher frequency being positive.

Figure 1 shows ^{63}Cu NMR spectra of CuI with and without MAS. The full width at half maximum in a static state is 2.5 kHz. Although the linewidth is reduced to some extent by spinning, spinning is not so effective as in CuBr and CuCl. The change of the peak position by spinning can be clearly seen in the spectra. Figure 2 shows the dependence of the peak position on the spinning rate. As the spinning rate becomes faster, the peak shifts towards upfield. The magnitude of this shift is about 10 ppm for spinning of 3 kHz.

We have observed ^{127}I NMR spectra of CuI also. The linewidth is little reduced by spinning, but the position changes depending on the spinning rate. The spinning-rate dependence of the peak position is plotted in Fig. 3. The peak posi-

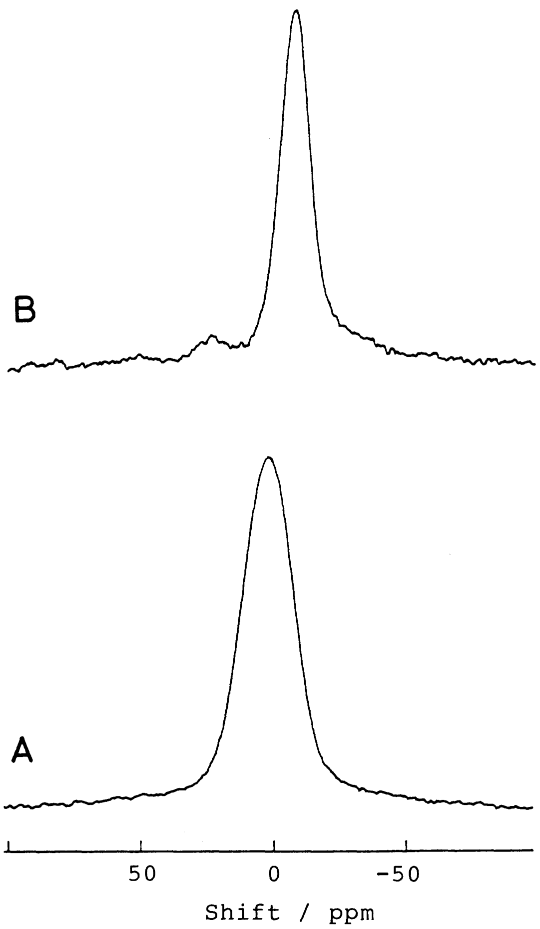

Fig.1. ^{63}Cu NMR spectra of CuI measured at 106.063 MHz (A) in a static state and (B) with MAS. The shift value is given with respect to CuCl spinning at 3.0 kHz. In (B), the spinning rate is 3.0 kHz, and humps on both sides of the center peak are spinning sidebands.

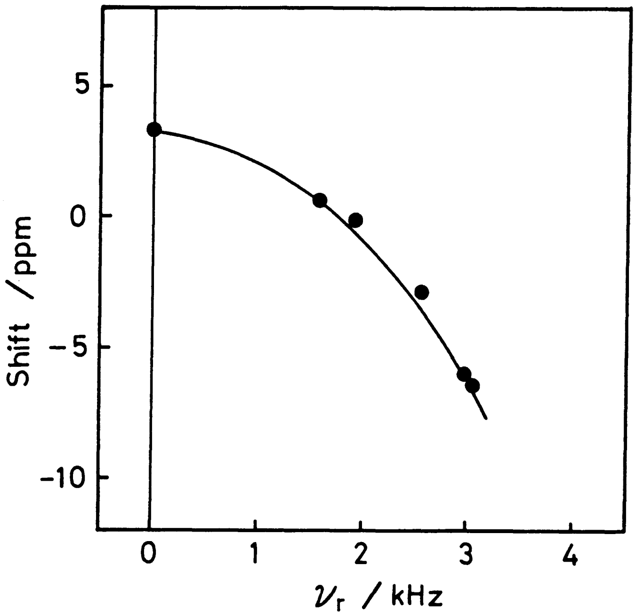

Fig.2. Dependence of the peak position on the spinning rate in ^{63}Cu NMR of CuI measured at 106.063 MHz. The shift value is given with respect to CuCl spinning at 3.0 kHz.

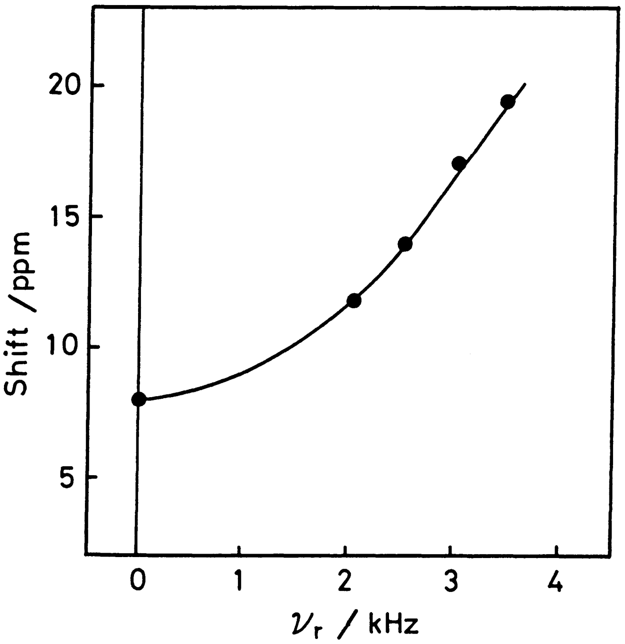

Fig. 3. Dependence of the peak position on the spinning rate in ^{127}I NMR of CuI measured at 80.073 MHz. The shift value is given with respect to KI.

tion shifts towards downfield as the spinning rate increases. The magnitude of this shift is equal to that in the ^{63}Cu NMR, but the shift direction is opposite.

As for CuBr and CuCl, the magnitudes of the shift in ^{63}Cu NMR are about 1 and 0.2 ppm, respectively, for the 3.0-kHz spinning, and the direction of the shift is the same as in CuI. On the other hand, the shift in ^{79}Br NMR of CuBr is about 1 ppm in the direction of downfield for the same spinning rate.

Our spectromrter is very stable, and the experimental error caused by the spectrometer is at most 0.05 ppm.$^{4)}$

Several mechanisms can shift the peak position theoretically, but we could not conclude the mechanisms which can explain the above spinning-rate-dependent shift until now. We have tried to apply some mechanisms, as described below briefly.

(1) In cuprous halides, a small amount of divalent cations, Cu(II), might be present, though monovalent Cu atoms, Cu(I), are dominant. Cu(II) has an unpaired electron. Spin-spin interaction between electron spins and nuclear spins might cause the shift. Knight shift is an example which is caused by the interaction with electron spins in conduction band,$^{5)}$ but this shift is not affected by spinning. Other mechanisms such as dipolar interaction with electron spins might shift the peak. However, if this interaction works, the signal suffers from severe line broadening. Experimentally, the linewidth is determined by the dipolar interaction between nuclear spins. Furthermore, the opposite shift direction between Cu and halogen nuclei rejects this mechanism.

(2) Bulk magnetic susceptibility caused by the unpaired electron on Cu(II) can shift the peak.$^{6)}$ In the MAS experiment, this effect vanishes if the spinning is fast enough. This mechanism can be ruled out again by the fact that Cu and halogen signals shift to opposite directions.

(3) Cu atoms are surrounded by four iodine atoms, which are quadrupolar nuclei. The dipolar interaction with quadrupolar nuclei might shift the peak position.$^{7)}$ Experimentally, we can check this possibility by observing the ^{23}Na nuclei in NaI. ^{23}Na has almost the same gyromagnetic ratio as ^{63}Cu, and the spin number is 3/2. We have measured the ^{23}Na NMR spectra of NaI, and the peak position did not change with the spinning rate within experimental error of 0.1 ppm. Consequently, this mechanism can be ruled out.

(4) CuI can absorb iodine, resulting in considerable electric conductivity.$^{8)}$ If the sample is electric conductor, the sample rotation in the high magnetic field might result in producing electric current in the small particles. This current will shield the magnetic field, causing upfield shift in the ^{63}Cu NMR. This possibility has been checked by observing the ^{63}Cu NMR signal of Cu metal powder, but the signal position is independent of the spinning rate. Furthermore, the ^{127}I and ^{79}Br NMR results exclude the possibility.

(5) Temperature rise due to the fast spinning might cause the shift. Indeed ^{13}C peaks of samarium acetate tetrahydrate shift depending on the sample temperature, which can be used as a thermometer.$^{9)}$ However, no temperature rise was observed in our probehead, which was checked by the above "thermometer." Furthermore, the peak position changed within a few seconds after the spinning rate was varied. This means that spinning directly influences the peak position.

(6) Second-order quadrupole interaction can shift the peak,$^{10)}$ if it exists.

Cuprous halides have a cubic lattice, and thus quadrupole interaction is negligible except for the region near to lattice defects. Experimentally, the line shape of NMR spectra is almost symmetric, and the contribution of the quadrupole interaction to the linewidth and to the line position is negligible. Furthermore, the magnitude of the second-order quadrupole shift does not depend on the spinning rate.10)

(7) The stress caused by the fast sample spinning might shift the peak. However, the mechanism which relates the stress to the shift is unclear. In any way, this mechanism is the only one that cannot be ruled out at the present stage.

Andrew et al.11) measured the ^{63}Cu and ^{65}Cu MAS NMR of the three cuprous halides, but they did not notice the spinning-rate dependence. The magnetic field they used was 1.14 and 1.32 T, which is much lower than the field we used (9.40 T). The spinning-rate-dependent shift might depend on the magnetic field.

At the present stage, we cannot conclude the mechanism of the above phenomena. We can only say that cuprous halides have a peculiar property which originates the spinning-rate-dependent shift. More detailed studies on the property are now in progress. If the property becomes clear, other compounds than cuprous halides might be found which show the spinning-rate-dependent shift.

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