

## CuF<sub>2</sub>의 펄스 핵자기공명 연구

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(1994. 6. 11 접수)

## Pulsed NMR Study of CuF<sub>2</sub>

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(Received June 11, 1994)

**요 약.** 펄스 핵자기공명 기법을 이용하여 상자성 물질인 CuF<sub>2</sub>를 조사한 결과 상온에서 <sup>19</sup>F 위치의 차이에 의한 확연히 구별되는 두 개의 공명선을 얻었다. 한 선은 진동수 이동이 거의 없었지만 다른 한 선은 진동수 이동이 심했다. 두 경우 모두 스핀-격자 완화시간( $T_1$ )이 짧지만 진동수 이동이 심한 경우에  $T_1$ 이 더 짧았다. 이는 두 경우에 대한 주위의 전자 환경이 다르기 때문으로 해석된다.

**ABSTRACT.** We have studied the paramagnetic CuF<sub>2</sub> using the techniques of pulsed nuclear magnetic resonance (NMR). The powder sample revealed two well-separated lines from the distinct <sup>19</sup>F sites at room temperature. One of the lines showed little frequency shift. However, the other showed a large frequency shift, suggesting electron transfers. Furthermore, the two sites have very short spin-lattice relaxation times ( $T_1$ ). The frequency-shifted site has the shorter  $T_1$  than the unshifted one, reflecting the difference of the electron environments of the two sites.

### INTRODUCTION

The importance of nuclear magnetic resonance in the study of the paramagnetic solids was first demonstrated by Bloembergen<sup>1</sup>. In the solids with dense paramagnetic ions, NMR would be unobservable in the absence of line-narrowing mechanisms due to the enormous dipole fields. In such systems, exchange interactions can result in "exchange narrowing"<sup>1,2</sup>. In addition, the strong exchange interactions may lead to magnetically ordered states at low temperatures. Line shifts and relaxations in the dense paramagnetic systems have been theoretically studied and measured mostly by continuous wave (cw) NMR<sup>3-8</sup>. Although a number of pulsed NMR studies on the paramagnetic impurity systems have been made<sup>9-15</sup>, the dense paramagnetic systems such as CuF<sub>2</sub> have not yet been extensively studied by pulsed NMR

and thus detailed spin-lattice relaxation studies have been lacking in those systems. In this work, we have employed the techniques of pulsed NMR to study the magnetic interactions and local environments in a paramagnetic solid, CuF<sub>2</sub>.

CuF<sub>2</sub> has a distorted rutile structure as shown in Fig. 1<sup>16</sup>. A Cu ion has two nearest neighbor F ions at a distance of 2.27 Å and four at 1.93 Å. This difference in the nearest neighbor distances is relatively large and can cause a considerable difference in the electronic environment for the two distinct sites of the F nucleus. From the magnetic susceptibility measurements, it is known to undergo an antiferromagnetic transition at 69 K<sup>17</sup>.

### EXPERIMENTAL

The powder sample used in this work was commercially available. The room temperature measu-

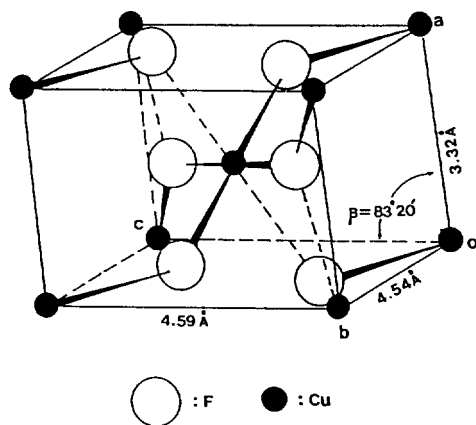


Fig. 1. The crystal structure of CuF<sub>2</sub>.

rements in this work were made at the <sup>19</sup>F frequency of 45 MHz using a pulsed NMR spectrometer set up in our laboratory. The home-built spectrometer includes a 12" Varian electromagnet and a pulse programmer operated by an IBM AT personal computer<sup>18</sup>. It provided a very short 90° pulse (2 μs) and receiver deadtime (5 μs), and an excellent signal to noise (S/N) ratio. Because of a very short decay constant of the FID (free-induction decay) signal, the solid echo sequence had to be used for the lineshape. The whole spectrum was too broad to obtain using a pulse modulated at a single frequency, at a single fixed magnetic field. Consequently, employing the point-by-point method<sup>19</sup>, the NMR magnetic field had to be swept for the whole spectrum. This means varying the NMR magnetic field for each data point in Fig. 2, keeping the NMR frequency at 45 MHz. The signal averaging was done using a Gould 400 digital storage oscilloscope interfaced to the personal computer. For the spin-lattice relaxation time measurements, the inversion recovery sequence with the solid echo detection was used at two peak positions. Since the CuF<sub>2</sub> compound gives relatively weak and broad resonance signals, much care had to be taken to avoid spurious background signals.

## RESULTS AND DISCUSSION

The <sup>19</sup>F lineshape obtained by the point-by-point method is shown in Fig. 2. It shows two well

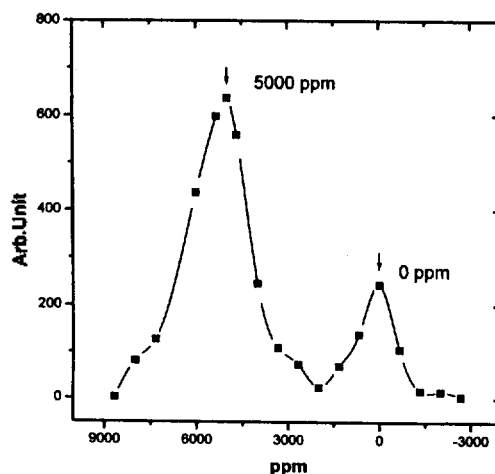


Fig. 2. The room temperature lineshape of CuF<sub>2</sub> at 45 MHz. The C<sub>6</sub>F<sub>6</sub> reference at 45 MHz corresponds to the external magnetic field of 11,230 G. The paramagnetically shifted line has a peak at 11,180 G.

separated lines. One of them is little displaced from the zero frequency determined from the C<sub>6</sub>F<sub>6</sub> reference, while the other shows a considerable shift. Considering the magnitude of the dipole fields, the fact that NMR signals are observed indicates the presence of the exchange narrowing, since otherwise the resonance lines would be too broad to observe.

A compound similar in composition to CuF<sub>2</sub>, MnF<sub>2</sub> has been investigated by cw NMR by Shulman and Jaccarino<sup>3</sup>. Even though it was in single crystalline form, the lines could be separated only depending on the crystal orientations. In this compound, the Mn-F distances, 2.11 Å and 2.14 Å, are little different. Shulman and Jaccarino explained the large frequency shifts in the compound by the fact that the Mn-F bond is not purely ionic, but is partially covalent. This causes a bonding electron to be transferred to the paramagnetic ion for some part of the time. The unpaired electron remaining on the F<sup>-</sup> ion produces its characteristic hyperfine field at the <sup>19</sup>F nucleus, causing a paramagnetic shift. This transfer of electrons is related to the superexchange mechanism<sup>20</sup> that leads to long range magnetic ordering. In MnF<sub>2</sub>, Shulman and Jaccarino were not able to measure the spin-lattice relaxation times.

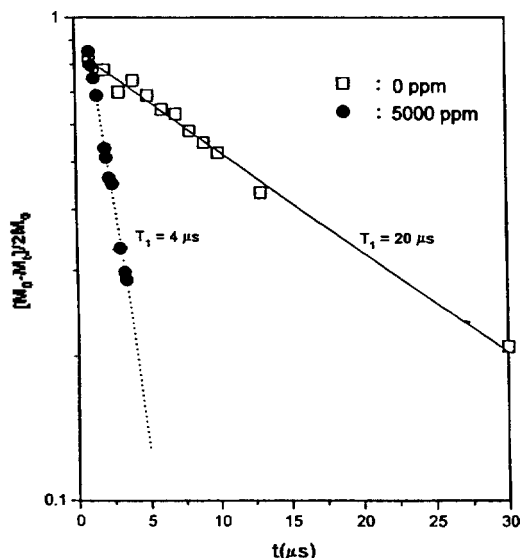


Fig. 3. The spin-lattice relaxation measurements of the two sites in  $\text{CuF}_2$ .

The two well-separated lines in  $\text{CuF}_2$  indicate that the two Cu-F bonds are of different character. The little-shifted line arising from the F nuclei with the longer 2.27 Å Cu-F bond distance corresponds to a nearly pure ionic character for the Cu-F bond. On the other hand, a shift of about 0.5% for the other line arising from the F nuclei of the shorter 1.93 Å Cu-F bond distance indicates the presence of a mixture of the covalent nature. This difference in the bonding nature seems to have much to do with the bond distances. When the Cu-F distance is larger, there will be less overlap of the electron clouds and thus the electron transfer will be hindered, leading to pure ionic character. The shorter bond distance, on the other hand, will make some electron cloud overlap possible, leading to partial covalent nature. In other words, the nature of the bonds in the metal fluorides must be a sensitive function of the bond distances. Our result for  $\text{CuF}_2$ , in which the two Cu-F bond distances show a considerable difference, seems to support this picture.

The spin-lattice relaxation time measurements for the two lines are shown in Fig. 3. It is seen that the two sites have very short, distinct time constants. The F nuclei with the shorter bond dis-

tance have a  $T_1$  of 4  $\mu\text{s}$ , while those with the longer bond distance have 20  $\mu\text{s}$ . This difference in  $T_1$  can be explained by the difference in the electron environments for the F nuclei. The F nuclei at the shorter bond site will experience an additional fluctuating field from the unpaired electron left by the electron transfer. Thus the electron transfer leads to an enhanced spin-lattice relaxation rate as well as a large line shift.

When the hyperfine interaction is the dominant term in the spin relaxations as in the  $\text{CuF}_2$  system, it has been shown<sup>3</sup> that the spin-lattice ( $T_1$ ) and the spin-spin ( $T_2$ ) relaxation times are of the same order and that they depend on the strength of the hyperfine interaction, *i.e.*, the components of the hyperfine interaction tensor. Then the extremely short relaxation times observed in this work indicates that the hyperfine interactions are unusually strong in the  $\text{CuF}_2$  system.

In summary, we have studied the dense paramagnetic solid system  $\text{CuF}_2$  by pulsed NMR. As a result, we have observed the role of the electron transfers in the line shifts and the relaxation rates.

#### ACKNOWLEDGEMENTS

The authors are grateful for the grants from the Korea Ministry of Education (BSRI) and the Korea Science and Engineering Foundation. Help from Baekwoon Foundation and the donation of the electromagnet by Prof. R. E. Norberg are also acknowledged. Assistance from J. E. Kim is acknowledged as well.

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