

## Superexchange in the Dense Paramagnet $\text{CuF}_2$

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We have studied the paramagnetic  $\text{CuF}_2$  using the techniques of pulsed nuclear magnetic resonance (NMR). The powder sample revealed two well-separated lines from the distinct  $^{19}\text{F}$  sites at room temperature and at 77 K. The distinct frequency shifts of the two lines appear to arise from 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.

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### I. Introduction

The importance of nuclear magnetic resonance in the study of the paramagnetic solids was first demonstrated by Bloembergen[1]. 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"[1, 2]. 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[3-8]. Although a number of pulsed NMR studies on the paramagnetic impurity systems have been made[9-15], the dense paramagnetic systems such as  $\text{CuF}_2$  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,  $\text{CuF}_2$ .

$\text{CuF}_2$  has a distorted rutile structure as shown in Fig. 1[16]. A Cu ion has F ions at a distance of 2.27 Å and at 1.93 Å in its vicinity. This difference in the bonding 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 measure-

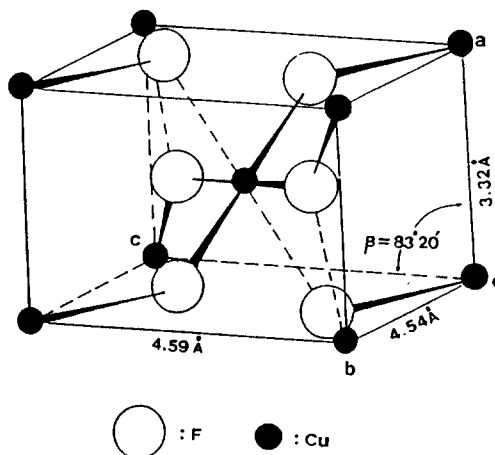


Fig. 1. The crystal structure of  $\text{CuF}_2$ .

ments, it is known to undergo an antiferromagnetic transition at 69 K[17].

### II. Experimental

The powder sample used in this work was commercially available. The room temperature and 77 K measurements in this work were made at the  $^{19}\text{F}$  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[18]. It provided a very short  $90^\circ$  pulse ( $2 \mu\text{s}$ ) and receiver deadtime ( $5 \mu\text{s}$ ), and an excellent signal to noise (S/N) ratio. Because of the 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[19], 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. The spin-lattice relaxation time measurements were taken with the solid echo detection at two peak positions. Since the  $\text{CuF}_2$  compound gives relatively weak and broad resonance signals, much care had to be taken to avoid spurious background signals.

### III. Results and Discussion

The  $^{19}\text{F}$  lineshapes obtained by the point-by-point method is shown in Fig. 2. They show two well separated lines. At room temperature, one of them is little displaced from the zero frequency determined from the  $\text{C}_6\text{F}_6$  reference, while the other shows a considerable shift. On the other hand,

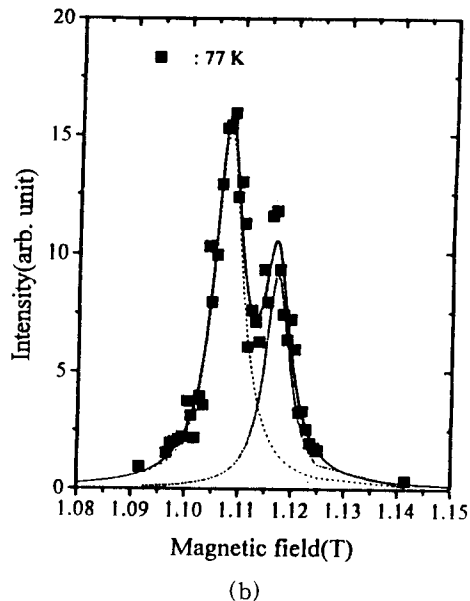
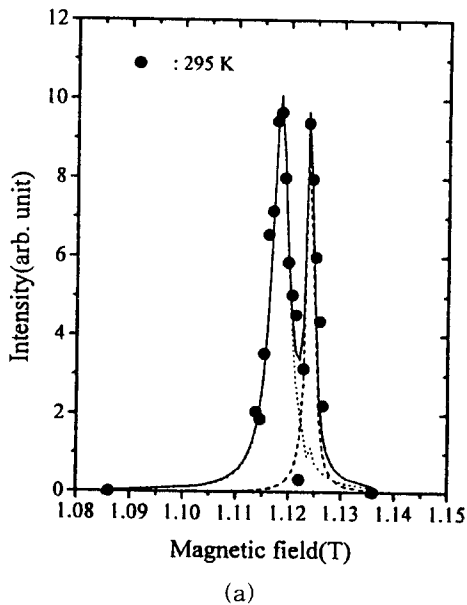


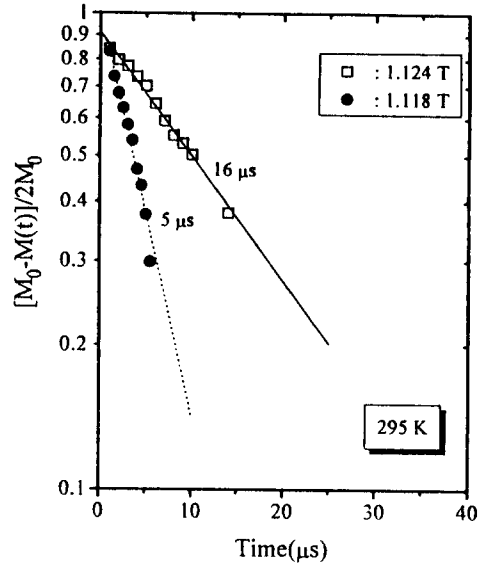
Fig. 2. (a) The room temperature and (b) 77 K lineshape of  $\text{CuF}_2$  at 45 MHz. The  $\text{C}_6\text{F}_6$  reference at 45 MHz corresponds to the external magnetic field of 1.1230 T.

both of them show significant shifts at 77 K. Considering the magnitude of the dipolar 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.

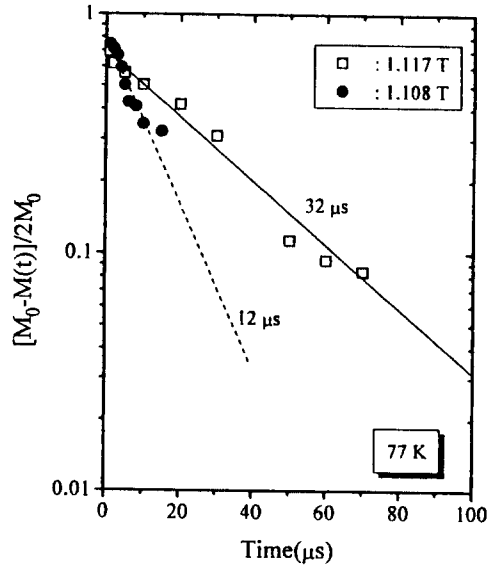
A compound similar in composition to  $\text{CuF}_2$ ,  $\text{MnF}_2$  has been investigated by cw NMR by Shulman and Jaccarino[3]. Even though it was in single crystalline form, the lines could be separated only depending on the crystal orientations. In this compound, the Mn-F distances, 2.11 Å and 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  $\text{F}^-$  ion produces its characteristic hyperfine field at the  $^{19}\text{F}$  nucleus, causing a para-

magnetic shift. This transfer of electrons is the superexchange mechanism[20] that leads to long range magnetic ordering. In  $\text{MnF}_2$ , Shulman and Jaccarino were not able to measure the spin-lattice relaxation times.

The two well-separated lines in  $\text{CuF}_2$  indicate the presence of two different Cu-F bonds. The difference in the bonding nature should have much to do with the bond distances. The less shifted line, corresponding to a more ionic character for the Cu-F bond, can be attributed to the F nuclei with the longer 2.27 Å Cu-F bond distance. On the other hand, the other line with a greater line shift indicates a more covalent nature, and is believed to arise from the F nuclei of the shorter 1.93 Å Cu-F bond distance. These assignments are based on the following arguments. 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 more 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. It is seen that the line shifts and the linewidths are much greater at 77 K than at room temperature. This can be understood as an indication of the temperature dependence of the hyperfine interactions of the F nuclei. 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 distance have a  $T_1$  of 5  $\mu\text{s}$ , while those with the longer bond distance have 16  $\mu\text{s}$  at room temperature. At 77 K, they are 12 and 32  $\mu\text{s}$ . This difference in  $T_1$  can be explained by the difference in the electron environments for the F nuclei. The F nuclei will experience a fluctuating magnetic field from the unpaired electron left by the electron transfer. Thus the electron transfer leads to an enhanced



(a)



(b)

Fig. 3. (a) The room temperature and (b) 77 K spin-lattice relaxation measurements of the two sites in  $\text{CuF}_2$ .

spin-lattice relaxation rate as well as a large line shift. It thus follows that the shorter bond site with more covalent nature will experience greater

fluctuating field and greater spin-lattice relaxation rate. It is also noticed that the relaxation times are longer at 77 K than at room temperature. There is no clear explanation for this until a more detailed temperature dependence study of the relaxation times is done. One possible explanation is the phonon contribution[12].

When the hyperfine interaction is the dominant term in the spin relaxations as in the  $\text{CuF}_2$  system, it has been shown[3] 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.

## II. Acknowledgements

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## 밀집된 상자성체 $\text{CuF}_2$ 의 초교환 상호작용

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상자성  $\text{CuF}_2$ 의  $^{19}\text{F}$ 에 대한 펄스 핵자기공명을 수행하였다. 분말시료에 대하여 상온과 질소온도에서 측정된 신호 양은 서로 다른 자리의  $^{19}\text{F}$ 에 대응하는 잘 분리된 두 개의 공명선으로 구성되었다. 두 공명선의 서로 다른 주파수 이동량을 구리원자로부터 불소 원자로 부분적으로 이동된 전자에 의한 기여로 해석할 수 있었다. 두 공명선은 모두 매우 짧은 스핀-격자 완화시간 ( $T_1$ )을 나타내었으며 더 큰 주파수 이동을 나타내는  $^{19}\text{F}$  공명선이 더 짧은 스핀-격자 완화시간을 보였다. 이를 두  $^{19}\text{F}$  자리 주위의 서로 다른 전자 환경이 반영되어 나타난 것으로 해석하였다.