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Electronic states of iron(III) complexes studied by nuclear forward scattering

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Introduction

The Mössbauer spectroscopy that uses the γ-ray source has been a powerful tool for inorganic chemistry, solid state physics and material sciences because it gives unique information on chemical bond and structure, valence states, and spin states. The nuclear forward scattering using the x-ray beam of the synchrotron radiation also gives the same information as that from the Mössbauer spectroscopy. The advantages of the nuclear forward scattering are (1) usually small amount of the sample is needed, (2) application of the perturbation such as magnetic field, photo radiations is easy, (3) polarization experiment is easily accessible.

The increased intensity of the synchrotron radiation has now enabled the realistic measurement of the nuclear forward scattering. While physical studies have been carried out for the rather hard materials such as oxides and metallic phases, the chemical investigations on the soft materials such as metal complexes and organometallic compounds have been scarcely reported. Thus we have been interested in the chemical applications of this method to structural inorganic chemistry.

Our most interest is to examine the possibility of the measurement on the sample containing the natural abundant iron. It is essential for developing the chemical applications because the chemical forms of enriched isotopes are limited and preparations of a serious of sample from such a source are usually time and money consuming. And if it is realized, the number of potential users will increase because the radioactive source will not be no longer needed. Thus our experiment has been aimed at this point. Our final purpose of this experiment is to obtain the electronic states of the iron(III) porphyrins. We have been studied the electronic state of iron(III) complexes of porphyrins. Recently we have been shown that some iron(III) complexes adopt the intermediate spin state S = 3/2 and some show spin crossover of S = 3/2 and 1/2 [1]. Two electron configurations are possible for the S=3/2 state and the existence of the both have been suggested from the NMR studies. Our final aim is to confirm this point using the nuclear forward scattering and to extend to the conditions of high pressure or photo irradiation.

Experimental

samples

Mohr's salt ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$) and iron alum ($Fe(NH_4)(SO_4)_2 \cdot 12H_2O$) were used as purchsed. The tetraphenylporphyriniron(III) chloride (Fe(tpp)Cl) was prepared according to the literature.

Measurements

The measurements were carried out at the AR NE-3 site using a ultra-high resolution X-ray spectrometer [2] at room temperature.

Results and Discussions

The spectrum for Moh's salt is shown in Fig. 1. The thickness of sample is 18 mgFe cm^{-2}, corresponding to 0.39 $mg^{57}Fe$ cm^{-2}. Although the spectrum was accumulated for about 6 h, the signal-to-noise ration is not so good. The spectrum shows a beat of about 50 ns and this agrees with the Mössbauer spectrum having a doublet with rather large quadrupole splitting. Although we have tried to measure iron alum with thickness of 25 mgFe cm^{-2} and Fe(tpp)Cl of 34 mgFe cm^{-2}, no effective scattering was observed. Our present results indicate that some spectra are measurable for ionic compounds even with the natural abundance though the thick samples are needed. The measurements for the molecular compounds with natural abundant iron seem to be difficult at least at room temperature. The results for iron alum was unexpected because iron(III) has a similar coordination sphere as that of iron(II) in Mohr's salt and the both are ionic compounds.

Although most of our attempts were unsuccessful, some examinations such as the measurements at the low temperature and improvement of the detection system would be needed.

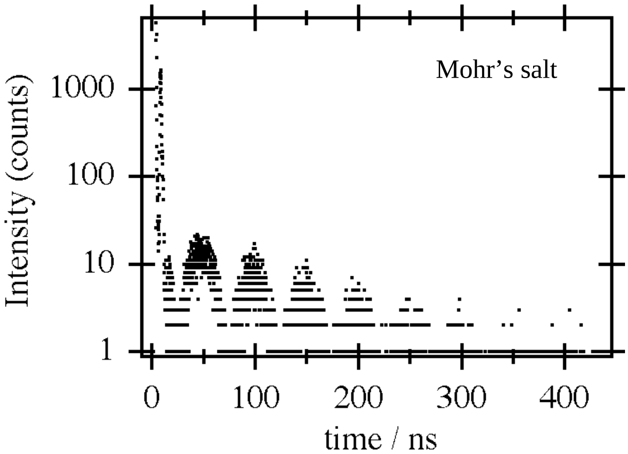

Fig. 1 Nuclear forward scattering spectra for Mohr's salt.

References

[1] T. Ikeue et al., Angew. Chem. Int. Ed. Eng., (2001), inpress, and references therein.
[2] T. Mitsui et al, Jpn. J. Appl. Phys., 36, 6625 (1997).

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