



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl19>

μ Sr Study of 1:1 Complex of bis(hexafluoroacetylacetonate) Manganese (II) with Diazodi(4-pyridyl)Methan as a Photo-Responsible Magnetic Coupler

Y. Ajiro ^a, T. Asano ^a, Y. Inagaki ^a, S. Karasawa ^b, N. Koga ^b, K. Nishiyama ^c, Y. Miyake ^c & K. Nagamine ^c

^a Department of Physics, Kyushu University, Fukuoka, 812-8581, Japan

^b Faculty of Pharmacy, Kyushu University, Fukuoka, 812-8582, Japan

^c Meson Science Laboratory, High Energy Accelerator Research Organization, KEK, Tsukuba, 395-0801, Japan

Version of record first published: 24 Sep 2006

To cite this article: Y. Ajiro, T. Asano, Y. Inagaki, S. Karasawa, N. Koga, K. Nishiyama, Y. Miyake & K. Nagamine (2000): μ Sr Study of 1:1 Complex of bis(hexafluoroacetylacetonate) Manganese (II) with Diazodi(4-pyridyl)Methan as a Photo-Responsible Magnetic Coupler, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 343:1, 103-108

To link to this article: <http://dx.doi.org/10.1080/10587250008023510>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

μ Sr Study of 1:1 Complex of bis(hexafluoroacetylacetonate) Manganese (II) with Diazodi(4-pyridyl)Methan as a Photo-Responsible Magnetic Coupler

Y. AJIRO^a, T. ASANO^a, Y. INAGAKI^a, S. KARASAWA^b, N. KOGA^b,
K. NISHIYAMA^c, Y. MIYAKE^c and K. NAGAMINE^c

^a*Department of Physics, Kyushu University, Fukuoka 812-8581, Japan*, ^b*Faculty of Pharmacy, Kyushu University, Fukuoka 812-8582, Japan* and ^c*Meson Science Laboratory, High Energy Accelerator Research Organization, KEK, Tsukuba 395-0801, Japan*

We apply muon spin relaxation (μ SR) technique to study the magnetic behaviors of the photosensitive molecular magnet, 1:1 complexes of bis(hexafluoroacetylacetonate) manganese(II), {Mn(hfac)₂} with diazodi(4-pyridyl)methane as a photoresponsible magnetic coupler. The μ SR time spectra have been collected before and after laser irradiation as a function of temperature from 290 K to 10 K and as a function of irradiation time during 30 hours. While we are not successful in detecting meaningful effects of irradiation at the present stage, we discuss potential usability of μ SR technique to reveal the expected unconventional feature of the photo-induced magnetic order.

Keywords: muon spin relaxation; photo-sensitive function; molecular magnet; magnetic order

INTRODUCTION

Recent progress of molecular synthetic technique has produced a rich variety of molecule-based magnets in a well controlled manner and developed an interesting new field of molecular magnetism. Here, we concentrated on the μ SR study of the molecule-based magnets with photo-sensitive function. The photo-sensitive effect in molecular magnets is attracting considerable interest from both fundamental and practical points of view, since photoresponsible function gives us a promising opportunity for the construction of molecular optomagnetic recording device.

Previous studies on the photo-sensitive molecular magnets are still in the early primitive stage in which macroscopic magnetization before

and after irradiation is compared between two cases. Microscopic research on such as mechanism of photo-induced transition and the dynamical behavior has not yet been explored. Magnetically sensitive μ SR technique is powerful to probe the static and dynamic magnetic behaviors from a microscopic point of view and has potential usability to investigate the molecular magnetism. [1]

SAMPLE AND MAGNETIC PROPERTY

Koga *et al.* [2-4] have succeeded in synthesizing newly the photosensitive molecular magnets, 1:1 complexes of bis(hexafluoroacetylacetonate) manganese(II), $\{\text{Mn}(\text{hfac})_2\}$ with diazodi(4-pyridyl)methane as a photoresponsible magnetic coupler, based on metal complexes with metal $3d$ and organic $2p$ heterospins. The obtained Mn(II) complex forms orange-coloured crystal. From X-ray crystal and molecular structure analyses it was shown that 1:1 complexes crystallize into two forms in which the two pyridine rings coordinate to metal ions in the *cis*- and *trans*-configuration to produce one-dimensional spiral and zig-zag chains of octahedral metal complexes, respectively. In the present work, we prepared *cis*-Mn(II) complex. Its crystal structure is shown in Fig.1.

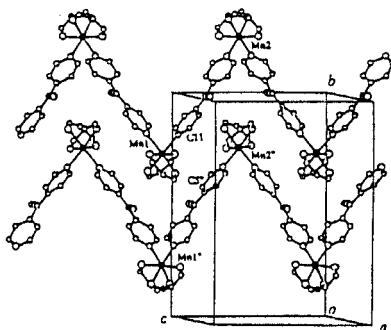


FIGURE 1 Crystal structure of *cis*-Mn(II) complex.

What is important in this molecular design is that a new bridging ligand, diazodi(4-pyridyl)methane has two kinds of functional groups, two pyridyl nitrogens and a diazo group. The former makes a polymeric chain structure by the ligation with metal ions, and the latter can be photolyzed to produce a magnetic carbene unit which plays a dual role of a triplet ($S = 1$) spin source and a magnetic coupling unit. Before irradiation, the chains are nothing but paramagnetic due to the magnetically isolated metal ions. Most importantly, upon irradiation,

metal ions are coupled magnetically via the photo-generated triplet radical centers to form one-dimensional magnetic chains.

Magnetic property of *cis*-Mn(II) complex was investigated before and after irradiation. Temperature dependences of molar magnetic susceptibility (χ) clearly showed that it becomes ferrimagnetic chains by the magnetic interaction between metal ions and generated carbenes after irradiation, while the complex is dilute metal-ion paramagnet before irradiation.

As an example, temperature dependence of χT is shown in Fig. 2. From the absolute value of the photo-induced magnetization, the formation of extended ferrimagnetic chains was estimated to contain over 200 units. More details of the results of *cis*- and *trans*-Mn(II) complex and the corresponding copper(II) complex should be referred to original papers by Koga's group. [2-4]

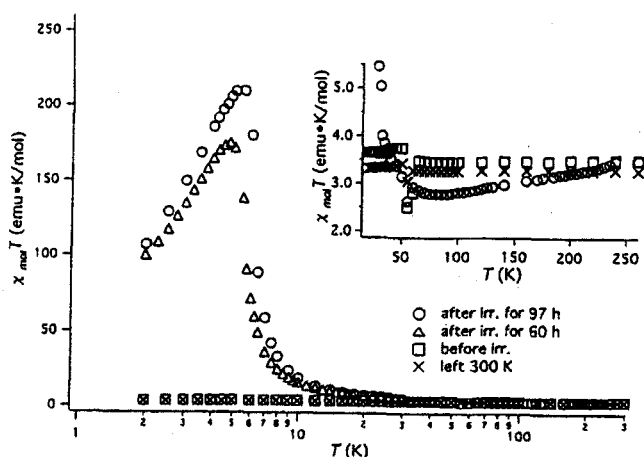


FIGURE 2 Temperature dependence of χT of *cis*-Mn(II) complex before and after irradiation.

μ SR EXPERIMENTS

It is very important to study the dynamics of above systems by using microscopic techniques. We have started the μ SR experiments on the laser-induced magnetism, including the first trial for the study of photoresponsible magnetic coupler mentioned above.

KEK group at Meson Science Laboratory, High Energy Accelerator Research Organization, has recently developed a new μ SR method combined with a pulsed laser, where the effect by laser can be probed in-site by muons implanted into irradiated specimen. [5] The μ SR experiments were performed on the π A beam port at KEK which provides a pulsed (50 ns width and 20 Hz repetition) beam of 100 % spin polarized muons with a momentum of 29 MeV/c. Irradiation was performed using pulsed YAG laser at wave length of 532 nm with a power range, 60 mW to 330 mW, monitored just in the front of the specimen.

As illustrated in Fig. 3, powdered sample of *cis*-Mn(II) complex (20 mm dia. and 1 mm thickness) was directly glued on the tilted cold Cu finger plate with thin Al covering foil. The laser was irradiated from the perpendicular direction to muon beam and the spot size was nearly equal to the sample cross section. Time spectra before irradiation were collected at zero and finite fields as a function of temperature.

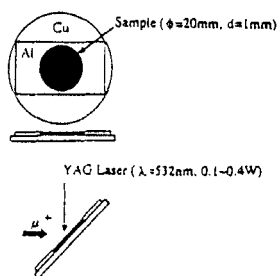


FIGURE 3 Geometry of the μ SR experiment under laser irradiation.

Figs. 4 and 5 show the time spectra collected before laser irradiation at transverse field $TF = 20$ G for room temperature and 9 K, respectively. From this oscillatory spectra which just correspond to the free Larmor precession of muon spin under the transverse field, we confirm there exist any static internal fields in the system. Figs. 6 and 7 are the zero field ZF time spectra collected before laser irradiation for room temperature and 9 K, respectively. At high temperature the time spectra has a Gaussian lineshape $A(t) = \exp(-\sigma^2 t^2)$ with slow damping due to random local fields from nuclear magnetic moments. With decreasing temperature, the lineshape changes from Gaussian to exponential damping $A(t) = \exp(-\lambda t)$, suggesting that spin fluctuation develops at low temperature. It reflects a paramagnetic relaxation as usual, indicating the compound is nothing but paramagnetic due to the magnetically isolated metal ions before irradiation. Then, in order to examined the effect of irradiation, we made a trial run to collect the time spectra at our lowest temperature of 10 K during 30 hours as a

function of irradiation time. We were not able to observe a meaningful change in time spectra at the present stage. The reason of this negative results is twofold. One is that our lowest temperature was not low enough to detect the effect of irradiation as expected from Fig.2 where a remarkable effect can be seen around 5 K. The other is that radiation did not penetrate sufficiently into the inside region where muons stopped and were limited to the surface region for which we observed a change in color into yellow.

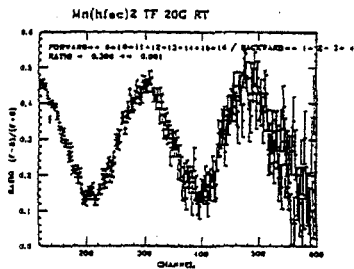


Fig. 4

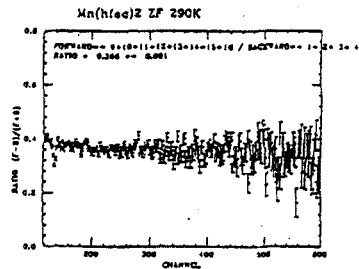


Fig. 5

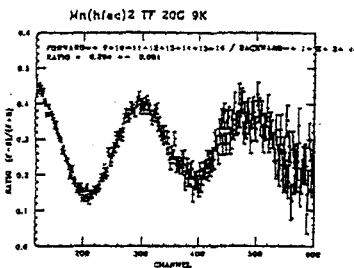


Fig. 6

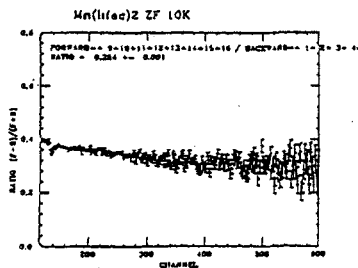


Fig. 7

FIGURE 4 Time spectra at transverse field TF = 20 G for room temperature.

FIGURE 5 Time spectra at transverse field TF = 20 G for 9 K.

FIGURE 6 Time spectra at zero field for room temperature.

FIGURE 7 Time spectra at zero field for 10 K.

DISCUSSION

While we are not successful in detecting definite meaningful effects of irradiation at the present stage, we are now proceeding the experiment after overcoming difficulties mentioned above. Here, we discuss potential usability of μ SR technique to reveal the expected unconventional feature of the photo-induced magnetic order. As mentioned above, the complex is nothing but paramagnetic due to the magnetically isolated Mn(II) ions before irradiation. Upon irradiation, metal ions are coupled magnetically via the photo-generated triplet radical centers in carben molecules. It goes without saying that the generated radicals are located randomly in the system. Therefore, the system becomes to be highly magnetically inhomogeneous after irradiation. In this sense, we expect unconventional feature of the photo-induced magnetic order. The anticipated magnetic order should be strongly inhomogeneous and spatially modulated, if any, including a possible coexistence of disordered and ordered regions. For such a magnetically inhomogeneous system, μ SR technique provides a powerful and unique method to probe the static and dynamic magnetic behaviors from a microscopic point of view. As demonstrated in some inhomogeneous systems [6], a time spectra may show an exceedingly different relaxation shape due to a spatially non-uniform wide distribution of the local internal fields in comparison with normal Gaussian and exponential damping. The method should be applicable to other interesting examples closely related with new molecular magnetism under laser-photon irradiation. Representatives are concerned with "Photoinduced magnetization of a Cobalt-Iron cyanide" and "Photocontrol of magnetic hysteresis in charge-transfer complex, MnTPP•TCNE". [7-8]

Acknowledgments We thank staff of Meson Science Laboratory at KEK for their technical support. This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Area from Ministry of Education, Science, Sports and Culture.

References

- [1] Y. Ajiro, *Proceedings of the International Workshop on JHF Science III*, 369 (1998).
- [2] N. Koga *et al.*, *Angew. Chem.* **108**, 755 (1996).
- [3] Y. Sano *et al.*, *J. Am. Chem. Soc.* **119**, 8246 (1997).
- [4] S. Karasawa, *et al.*, to be published.
- [5] K. Shimomura *et al.*, *Proceedings of the International Workshop on JHF Science III*, 282 (1998).
- [6] K.M. Kojima *et al.*, *Phys. Rev. Lett.* **79**, 503 (1997).
- [7] O. Sato *et al.*, *Science* **272**, 704 (1996).
- [8] K. Nagai *et al.*, *Solid State Commum.* **102**, 809 (1997).