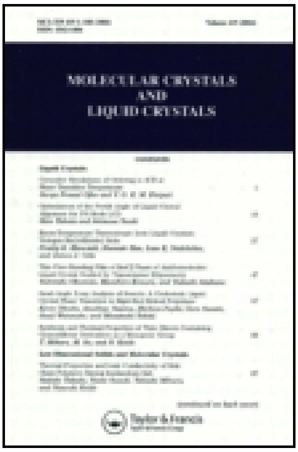

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Published online: 02 Sep 2013.

Mol. Cryst. Liq. Cryst., Vol. 578: pp. 44–49, 2013

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.803909

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Photoirradiation Effect on Magnetic Susceptibility in Organic Superconductors

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Photoirradiation effects on magnetic susceptibility are studied in organic superconductors of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br and β-(BEDT-TTF)$_2$I$_3$ (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene), for which we have reported photoresponses of the electrical conductivity elsewhere. With photoirradiation by cw visible laser light, the diamagnetic susceptibility originating from Meissner effect is reduced, indicating that the percentage of superconducting volume decreases with photoirradiation. These results agree with the ones of the time-resolved photoresponse measurements of the electrical conductivity using pulsed laser light.

Keywords Organic charge transfer complex; Meissner effect; photoexcitation dynamics; superconductivity

1. Introduction

Control of material properties by using external perturbations such as photoirradiation and external electric fields has been the subject of active investigation for the development of innovative optoelectronic functional materials [1]. Organic conductors have recently attracted much attention as such potential optoelectronic materials. This is because organic conductors can show phase transitions among a variety of phases including a superconducting state, and there is often a competition between the phases [2]. Recently, a photoinduced phase transition from insulating phase to metallic phase has been demonstrated in crystals of organic conductors by the irradiation of a pulsed laser light. Femtosecond pump-probe spectroscopy and time-resolved photoresponse measurements of electrical conductivity have shown that the metallic state is transiently produced after the photoexcitation of the crystals in insulating phase [3–6]. In addition to the photoirradiation, the application of electric fields can also be a tool to induce the transition from the insulating phase to the metallic phase. For example, electric-field-induced insulator−metal transition has been reported in the organic Mott insulator deuterated κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br [7], where BEDT-TTF represents bis(ethylenedithio)tetrathiafulvalene.

The realization of a photoinduced conversion of normal material to superconductor is, in particular, the most challenging problem. However, the possibility of the photoinduced conversion from states of normal electrical resistivity to a superconducting state

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in organic conductors is still open question. In a strategy toward realizing photoinduced superconductivity, understanding of the photoresponse of organic conductors showing superconductivity, namely organic superconductors, is indispensable.

One of remarkable characteristics of superconductors is zero electrical resistance. Time-resolved photoresponse measurements of electrical conductivity in the organic superconductors hydrogenated κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, denoted by κ-Br, and β-(BEDT-TTF)$_2$I$_3$, denoted by β-I$_3$, have been performed with photoexcitation using a nanosecond pulsed laser light [8,9]; these compounds show a transient increase of resistance following photoexcitation, namely the decrease of superconductivity.

The so-called Meissner effect is also a remarkable characteristic of superconducting state. This effect states that magnetic field is expelled from superconductors, and consequently one can observe a diamagnetism in superconducting states in comparison with those in normal states. Then, measurements of photoirradiation effects on magnetic susceptibility can be powerful techniques to investigate the photoinduced superconductivity as well as the photoresponse of superconductors. Moreover, the investigation of photoirradiation effects on magnetic property is expected to be complementary to the results related to the measurement of the electrical conductivity. We have thus developed an experimental system for the study of photoirradiation effects on magnetization of molecular materials. Here, we report photoirradiation effects on static magnetic susceptibility of κ-Br and β-I$_3$.

2. Experimental

Single crystals of κ-Br and β-I$_3$ were prepared according to the literature.[10,11] Samples used in the measurements were polycrystalline granules. Magnetic moment of the samples in the presence of magnetic fields was measured with a magnetometer using a SQUID detector (Quantum Design, MPMS-7) at the Instrument Center, the Institute for Molecular Science. The sample temperature was raised after zero-field cooling to 2–4 K. Actually, a remnant field of the superconducting magnet of the magnetometer existed in the cooling, evaluated to be smaller than 5 Oe.

For the measurement of the magnetic moment of the sample under photoirradiation, we assembled a sample rod which consisted of a sample holder made from quartz and optical fibers for delivery of laser light. In the sample holder, the sample was contained in a void formed between polished ends of linearly-aligned two quartz rods. One of the quartz rods was used as a light guide. The quartz rods and the sample were enclosed by an outer quartz tube with a diameter of 5 mm. Because of the diamagnetism of quartz, the sample holder without the sample yielded a paramagnetic signal. The paramagnetic contribution from the sample holder was subtracted from observed magnetic moment for correction. A cw diode laser light at 447 nm was used for photoirradiation. This wavelength is close to an intramolecular absorption band of BEDT-TTF [12]. Laser light intensity was adjusted by using a variable neutral density filter.

3. Results and Discussion

κ-Br and β-I$_3$ are important targets because they have been extensively studied as prototypes of organic superconductors, and valuable suggestions for the elucidation of superconducting mechanism have been obtained. The superconducting transition critical temperature (T_c) of κ-Br at ambient pressure is $\sim$11 K (Fig. 1(a)) [10], while β-I$_3$ shows two different T_cs (Fig. 1(b)), that is, higher T_c (high-T_c) is observed at $\sim$7.5 K and lower T_c (low-T_c)

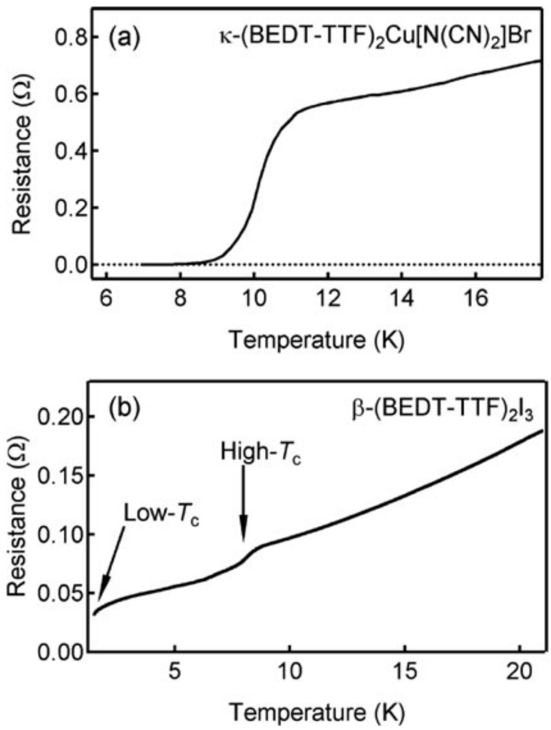

Figure 1. Resistance of single crystals of κ-Br (a) and β-I_3 (b) as a function of temperature. High-T_c and Low-T_c in β-I_3 represent two different superconducting transition critical temperatures. The data are the same as the ones given in Refs. [8] and [9].

is located at the temperature lower than 2 K. In the superconducting phases of κ-Br and β-I_3, the resistance of the sample is transiently increased by photoirradiation, showing a decay to the original resistance without photoirradiation on a millisecond timescale [8,9]. This observation suggests the decrease of the percentage of superconducting volume by photoirradiation. However, these two salts show different temperature dependences of the relaxation time from each other.

Temperature dependences of the magnetic moment of κ-Br measured at 20 Oe with photoirradiation at different intensities are shown in Fig. 2. The weight of the sample was 3.7 mg. In each run of the measurements, temperature was increased under photoirradiation from 4 K to 16 K, which is higher than T_c. Note that temperature was not raised by the photoirradiation. Without photoirradiation, the onset of the diamagnetic susceptibility occurred at 11−12 K, in agreement with a previous study [13]. The onset of the diamagnetic susceptibility shifts to lower temperatures with the increase of irradiation light intensity. Photoinduced change of the magnetic moment at 8.5 K as a function of irradiation light intensity is plotted in Fig. 3. The diamagnetic susceptibility originating from Meissner effect was reduced by photoirradiation, and the photoinduced change shows a nearly linear dependence at low irradiation light intensities. In summary, the photoirradiation effect observed in the magnetic susceptibility shows the decrease of the superconducting volume, and these results are consistent with the ones obtained from the time-resolved photoresponse measurements of the electrical conductivity.

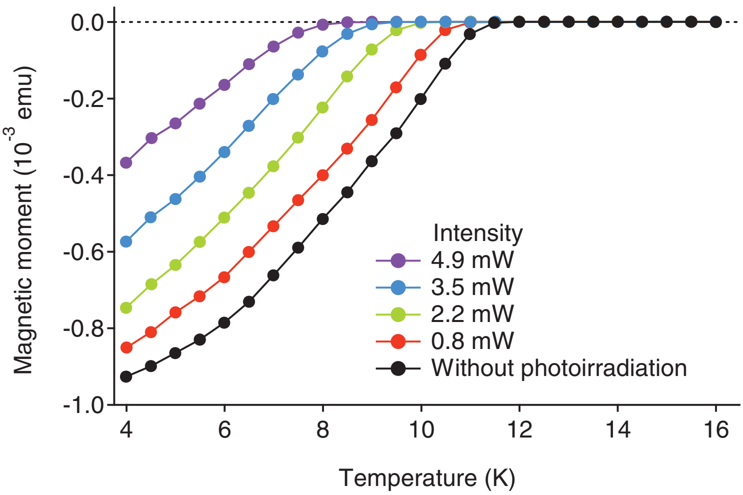

Figure 2. Temperature dependences of magnetic moment measured with different photoirradiation intensities in κ-Br.

Temperature dependences of the magnetic moment of β-I_3 have also been observed at 30 Oe. The results are shown in Fig. 4. The weight of the sample was 2.1 mg. In each run of the measurements, photoirradiation was started at 2 K, and then temperature was increased to 20 K. The onset of the diamagnetic susceptibility appeared at ~7 K, in agreement with the high-T_c superconducting transition temperature observed in the resistance. The photoinduced reduction of the diamagnetic component was observed, and these results are consistent with the ones of the time-resolved photoresponse measurements of the electrical conductivity. The photoirradiation effect was enhanced with an increase of the irradiation light intensity. It is likely that the onset temperature of the high-T_c phase scarcely shifts

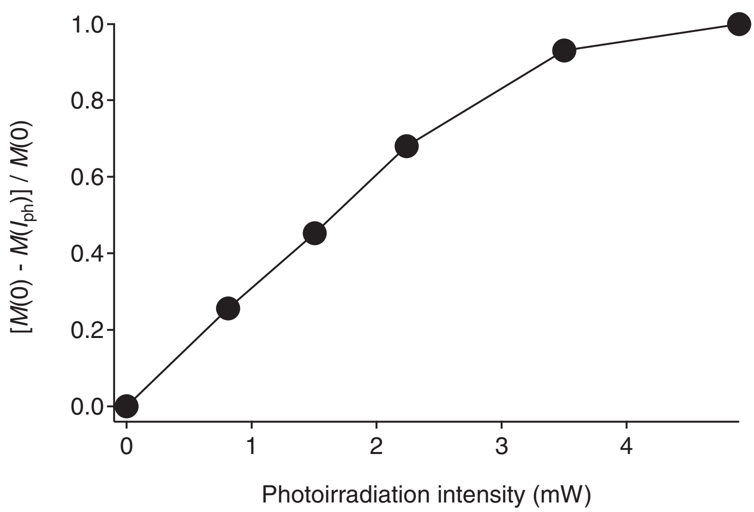

Figure 3. Photoinduced change of the magnetic moment ($M(I_{ph})$) at 8.5 K as a function of photoirradiation intensity (I_{ph}) in κ-Br.

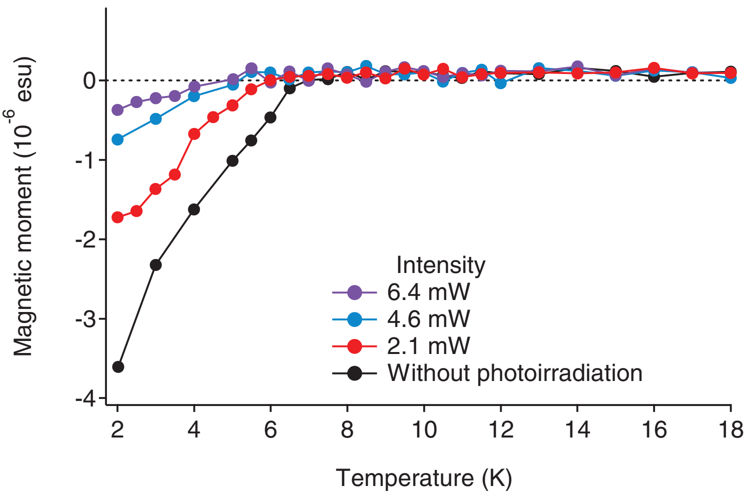

Figure 4. Temperature dependences of magnetic moment measured with different photoirradiation intensities in β-I_3.

with a change in irradiation light intensity. This behavior is different from the photoinduced shift of the onset observed in κ-Br. Our results consequently indicate that the difference exists not only in the temperature dependence of the relaxation time of the photoinduced change of electrical conductivity but also in the photoresponse of magnetic susceptibility.

4. Summary

We have measured photoresponse of magnetic susceptibility of κ-Br and β-I_3. The diamagnetic component originating from the Meissner effect is reduced by photoirradiation of cw visible laser light in both salts. These observations indicate that the superconducting volume is reduced by photoexcitation, consistent with the results obtained from the time-resolved photoresponse measurements of the electrical conductivity.

Acknowledgments

N. O. was Guest Professor at Institute for Molecular Science (IMS) in Okazaki from April 2010 to March 2012. N. O. and T. I. greatly appreciate the Joint Studies Program (2010–2012) of IMS for the support of the collaboration work.

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