OPTICAL AND ESR STUDIES ON AN IR ABSORPTION BAND

IN CsI:Na AFTER X-RAY IRRADIATION

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We have studied the nature of the defect giving rise to a near IR absorption
band (717 nm) in X irradiated CsI:Na by measuring its linear dichroism, its
magnetic circular dichroism and its change due to the resonance microwave.
The defect ($g_{||} = 1.96$, $g_{\perp} = 2.23$ with axis near <100>) involves a Na^+ ion
and an excess electron.

1. INTRODUCTION

X-ray irradiation at low temperature usually
creates in alkali halide crystals stable elec-
tron and hole centers at the same time, like F
and V_k centers. This is not the case in pure
CsI crystals, even below 4.2 K.

When CsI doped with NaI is irradiated at low
temperature, two optical absorption bands
appear at 408 and 717 nm[1]. The former one
which is independent of doping impurities is
attributed to the V_k center[2]. The latter near
infrared absorption whose excitation leads to
intrinsic recombination luminescence was
supposed to be due to an electron trap such as
Na^0 [1].

ESR may be one of the best tools to study
the origin of this absorption band as well as
its atomic structure. However, ESR observed so
far in CsI:Na with direct detection technique
is only that of the V_k center[2]. In order to
study the origin of this absorption, optical
properties of this band including the magnetic
circular dichroism (MCD) have been studied. We
found ESR with X-band microwaves (9.1 GHz) by
an optical detection technique in which the
microwave induced change of MCD has been moni-
tored.

2. EXPERIMENTAL

The optical absorption spectrum and its
linear dichroism at 4.2 K together with the

excitation spectrum for the 338 nm intrinsic
recombination luminescence[3] around the absorp-
tion band are shown in Fig. 1. The total area
of the IR absorption band is about 5 times as
large as that of 408 nm band. The linear di-
chroism, the relative difference of absorption
coefficients $\Delta\sigma = (\sigma_{||} - \sigma_{\perp})/(\sigma_{||} + \sigma_{\perp})$, has
been measured after the bleaching with 660 nm
and 770 nm light linearly polarized parallel to
one of the <100> crystal axes. There is no
dichroism apparently in both cases within 5% of
experimental error. The excitation spectrum is
very similar to the absorption spectrum. The
excitation bleaches with equal rates both IR
and V_k absorption bands.

The MCD spectra are shown in Fig. 2 for the
case in which the magnetic field is applied
parallel to <100> axis; similar results are
obtained when the magnetic field is parallel to
<111>. They are derivative type curves of the
absorption band and they display the same shape
over all the measured temperature and magnetic
field region. The dependence of the MCD inten-
sity at 680 nm on the temperature and the mag-
netic field are shown in Fig. 3. The result
indicates that the MCD of this band is deter-
mined by the so-called paramagnetic term, that
is, spin polarization in the ground state.

When the resonant microwave field H_1 is
applied at 1.5 K to the crystal with a static
magnetic field, the MCD decreases towards
zero, since the microwave bleaches the ground
state spin polarization; the MCD decreases up
to about 20% of its initial value showing a
characteristic saturation with increasing
microwave power. Since the MCD is determined

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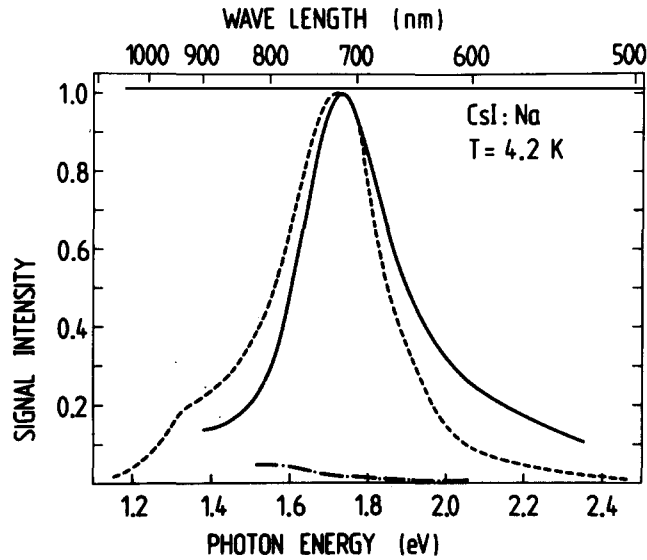Osaka City University, Osaka (Japan)

Fig. 1

Solid, dashed and dotted lines show optical absorption (in arbitrary unit), its linear dichroism $(\sigma_{||} - \sigma_{\perp})/(\sigma_{||} + \sigma_{\perp})$, and excitation spectrum (a.u) of the 338 nm intrinsic recombination luminescence at 4.2 K, respectively, after X-ray irradiation on CsI:Na crystal. Lower and higher energy sides of the absorption measurement are limited by the spectrometer and the glass filter used to cut the luminescence.
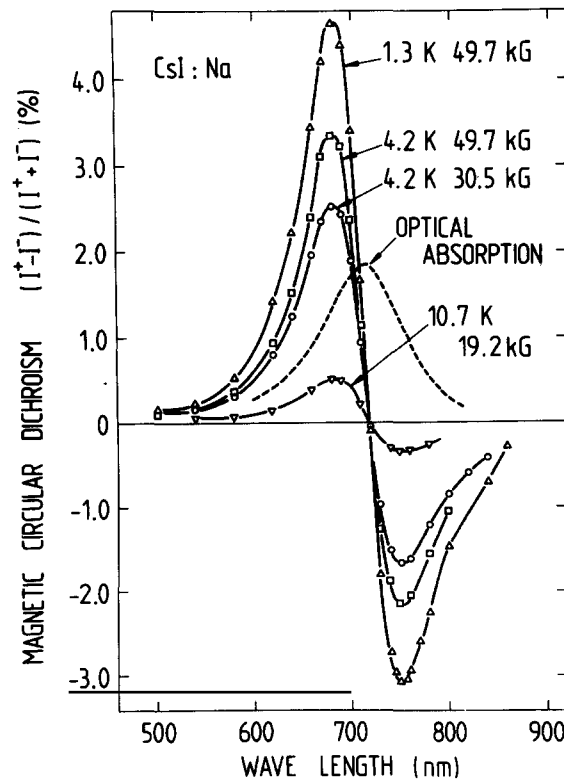

Fig. 2

Magnetic circular dichroism of the IR absorption band on Fig. 1 at several temperatures and magnetic fields.
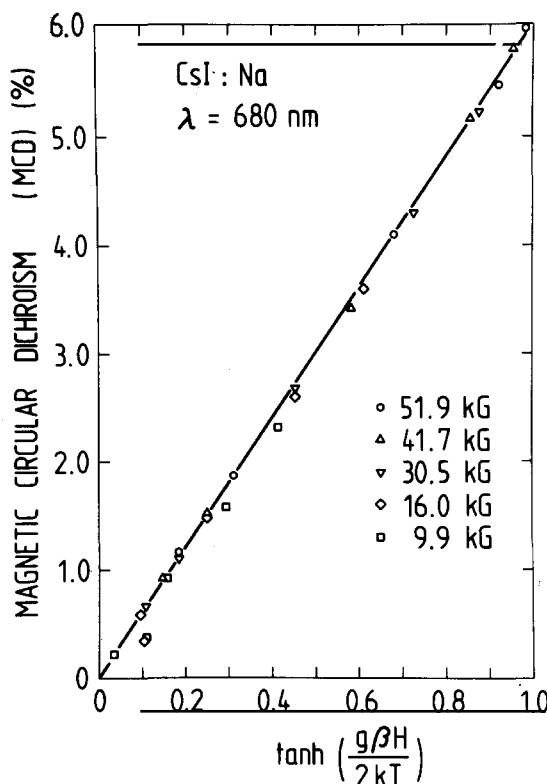
Fig. 3

The dependence of the magnetic circular dichroism intentity at
680 nm on the temperature and on the magnetic field which is applied
parallel to <100>.

by spin polarization in these experimental
conditions for ESR, one can obtain an ESR
spectrum as $[MCD(H_1 = 0) - MCD(H_1)]/MCD(H_1 = 0)$ as
shown in Fig. 4 (a), (b) when the magnetic
field is applied parallel to the <100> and
<111> directions, respectively; the MCD is
monitored at 680 nm to give the spectra of
Fig. 4.

When the magnetic field is applied parallel
to the <111> direction, the overall features
of the ESR spectrum are symmetric around the
peak position. When the field is parallel to
<100>, the ESR is asymmetric and shows another
peak on the higher field side. The similar
spectrum has been obtained at 4.2 K. These
results, together with the spectrum obtained
with the magnetic field parallel to <110>,
show that the symmetry of the center is lower
than O_h and that its symmetry axis is parallel
or near to the <100> axis.

3. DISCUSSION

ESR spectra have been analyzed by means of
the method of moments by assuming the symmetry
axis parallel to the <100> axis and the axial
symmetric spin Hamiltonian

$$\mathcal{H} = \beta[g_{||} H_z S_z + g_\perp (H_x S_x + H_y S_y)]$$
$$+ \sum_i \vec{I}_i \cdot \tilde{A}_i \cdot \vec{S} \qquad (1)$$

where the last term is the hyperfine inter-
action with nuclei. Furthermore, we tentati-
vely assume isotropic optical absorption
coefficient, since there was no linear
dichroism. One can obtain $g_{||}$ and $g_\perp$ of
1.97 ± 0.02 and 2.23 ± 0.02, respectively,
from the first moments of the ESR spectra
under three configurations of the magnetic
field. Peak positions according to these
g-value are shown in Fig. 4 (a), (b) by solid
arrows.

The following facts suggest that the center
is associated with an electron; the center is
created by X-ray together with the V_k center
and the excitation of this IR band enhances
the intrinsic recombination luminescence and
bleaches the V_k and IR absorption bands. On
the other hand, one may imagine an hole center
from the rather large positive g-shift of $g_{||}$.
One should check the possibility that the IR
absorption band is produced by the overlap of
two absorption bands due to electron and hole

Fig. 4

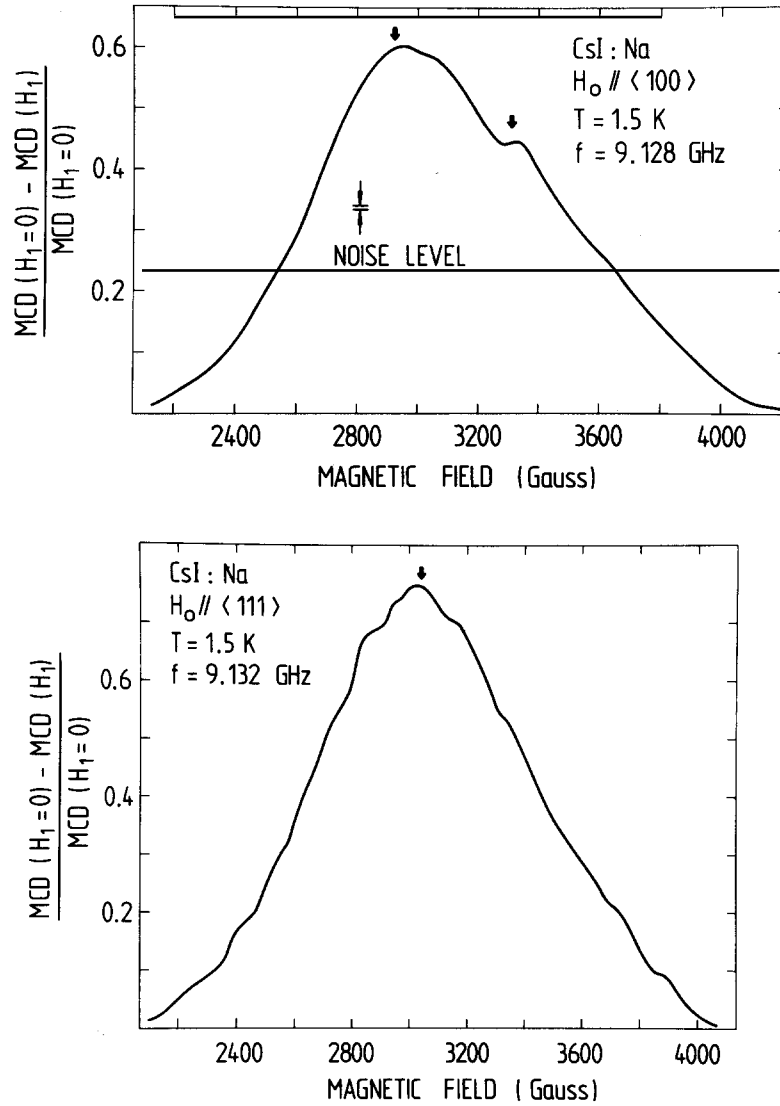ESR spectra (a) and (b) obtained by means of the optical detection
technique at 1.5 K with the magnetic field parallel to <100>
(f_o = 9.128 GHz) and to <111> (9.132 GHz), respectively.

centers. The following facts suggest that the
absorption band, or at least most of it, is
due to one center only : (1) the excitation
spectrum is very similar to the absorption
band; (2) the MCD spectrum is independent of
the magnetic field and of the temperature;
(3) the ESR spectra obtained by monitoring MCD
at 630 and 800 nm are the same as those at
680 nm; (4) the saturation recovery curves of
the ESR signal are the same at several magnetic
fields over the ESR spectrum.

If the center moves by changing the direc-
tion of its symmetry axis, the absence of
linear dichroism does not indicate necessarily
an isotropic absorption coefficient. It is

possible to fit the first moments within experi-
mental error by using the anisotropic absorption
coefficients within the region of $|\Delta\sigma| < 0.4$;
the set of g-values is the same as in the
previous case. The second moment analysis has
been tried with the spin Hamiltonian of eq. (1)
and the assumption that the principal axes of
the hf tensor are the same as those of the
g-tensor. In this analysis, theoretical values
can fit the experimental ones only when one
introduces the anisotropy of the absorption
coeffieicnet. Our assumptions such as isotropy
of the absorption coefficient, and the possibi-
lity of minor contribution from another center,
must be checked by more precise experiments.
Furthermore, temperature dependence of ESR

including relaxation time would be interesting to see dynamical effects of this center.

4. CONCLUSION

A paramagnetic center associated with the Na^+ ion and an electron gives the IR absorption band peaked at 717 nm produced by X-ray in CsI:Na. The center has a symmetry lower than O_h, the principal axis lying around <100> and

the g-values being $g_{||} = 1.97 \pm 0.02$ and $g_{\perp} = 2.23 \pm 0.02$. This indicates that the paramagnetic spin is not simply due to a 3s electron on a Na^+ ion.

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