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Optical detection of impurity NMR in the magnetic circular dichroism of F centres in alkali halide crystals

D M Hofmann†, N G Romanov‡ and J-M Spaeth †

† Fachbereich Physik, Universität Paderborn, D-4790 Paderborn, Warburger Strasse 100A, Federal Republic of Germany

‡ A F Ioffe Physical Technical Institute, Russian Academy of Science, 194021 St Petersburg, Russia

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Abstract. Nuclear magnetic resonance of thallium impurities has been detected by monitoring the magnetic circular dichroism of the absorption of F centres produced by room temperature x-irradiation under optical pumping conditions in Tl-doped KCl and RbCl crystals. In addition, electron nuclear double resonance signals of the F centre ligands were detected without microwaves. The observed effects are caused by hyperfine coupling of the F centres to the surrounding nuclei. F centres are probably produced with a spatial correlation to the thallium impurities.

1. Introduction

Electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) in the ground and relaxed excited states of F centres have been detected optically by monitoring changes of the magnetic circular dichroism of the optical absorption (MCDA) several times in the past (Mollenauer and Pan 1972, Mauser *et al* 1977, Winnacker *et al* 1977 and references therein). Jaccard *et al* (1975, 1978) studied optically detected EPR (ODEPR) and optically detected ENDOR (ODENDOR) of F centres using the luminescence technique. Hyperfine coupling between the nuclear spins and the electronic spins and cross relaxation effects made it possible to observe ENDOR without microwaves (CRENDOR) of Tm^{2+} in CaF_2 (Diekmann *et al* 1983).

In the present paper we report on a new effect, the detection of thallium impurity nuclear magnetic resonance (NMR) by monitoring the MCDA of F centres under optical pumping conditions in thallium-doped alkali halides, as well as on the observation of ligand ENDOR of F centres at low concentrations under the same experimental conditions. For both observations no microwaves are needed.

2. Experiment

Alkali halide single crystals (KCl, KBr) doped with either thallium or thallium and silver (each to about 0.5% in the melt) have been grown by the Bridgman technique. The crystals were irradiated with x-rays (60 kV, 30 mA, 30 min) to create F centres in concentrations of approximately 1×10^{16} cm^{-3} at room temperature.

Optical absorption, MCDA, ODEPR and ODENDOR were measured at 1.5 K with a computer-controlled spectrometer described elsewhere (Ahlers 1985). For the measurements the light of a 150 W tungsten lamp was filtered with a double-grating monochromator ($\frac{1}{4}$ m Jarrel–Ash). Circularly polarized light was generated by the combination of a piezo-elastic quartz modulator and a linear polarizer under 45°. It was modulated with 27 kHz.

3. Results and Discussion

In the spectral range of 2.0 to 3.0 eV the MCDA spectrum of the thallium-doped KCl crystals irradiated with x-rays at 300 K is a superposition of two overlapping bands, one originating from the F centres and one from a transition of $Tl^0(1)$ centres (figure 1, curve (a)), which consists of a paramagnetic Tl^0 atom ($6s^26p^1$ configuration) next to a Cl^- vacancy. Two further optical bands of $Tl^0(1)$ centres, explained by a crystal field model for the 6p multiplet, occur at lower photon energies (Ahlers *et al* 1983, 1984). Optical pumping of the MCDA of the F centres is achieved by increasing the intensity of the measurement light, which results in a decrease of the intensity of the MCDA. This optical pumping effect is caused by a spin memory loss in the recombination cycle in the excited states of the F centre and is described in detail by Mollenauer and Pan (1972). Under optical pumping conditions the electron spin polarization is not in thermal equilibrium which makes it possible to observe EPR transitions of other defects in the MCDA of the F centre without the application of a microwave field in the presence of cross relaxation effects. Similarly to previous investigations (Romanov *et al* 1989, Baranov *et al* 1991) EPR lines at 1.8 T of Tl^{2+} centres and at 2.8 T of $Tl^0(1)$ centres have been observed as an increase in the MCDA of the optically pumped F centres (figure 2). This observation of EPR lines of Tl^{2+} and $Tl^0(1)$ centres was explained as being due to cross relaxation effects between the optically pumped F centres and the Tl^{2+} and $Tl^0(1)$ centres, respectively. For 1.8 T and 2.8 T there is an energy resonance between the electronic Zeeman levels of F centres and those of the Tl^{2+} and $Tl^0(1)$ centres (Romanov *et al* 1989, Baranov *et al* 1991). Further EPR signals of an as yet unidentified defect have been observed in the low-field range (see figure 2).

The application of a radiofrequency (RF) field to the sample while monitoring the intensity of the optically pumped MCDA of the F centre at a fixed static magnetic field resulted in two types of effects.

(i) The MCDA increased by 0.25 to 0.5% at RFs that corresponded to the ENDOR frequencies of the first ^{39}K and second ^{35}Cl shells of the F centres (figure 3). Also the distant ENDOR signals of ^{35}Cl and ^{37}Cl have been detected at their Larmor frequencies. The chemical identities of the nuclei observed have been established by the measurement of their ENDOR frequencies at different magnetic fields (field shift method, Seidel (1961)). The decay time of the ENDOR signals after switching off the RF was of the order of 1 s.

(ii) In the KCl crystals doped with thallium the MCDA decreased by about 1.5% at the two RFs that correspond to the ^{203}Tl and ^{205}Tl Larmor frequencies (figure 4). Their relative signal intensities correspond to the natural abundance of the two thallium isotopes. The decay time of the signal after switching off the RF was of the order of a few hundred seconds (200–400 s), which explains the 'exponential' signal decay towards higher frequencies in figure 4. The linewidth of both ^{203}Tl and ^{205}Tl

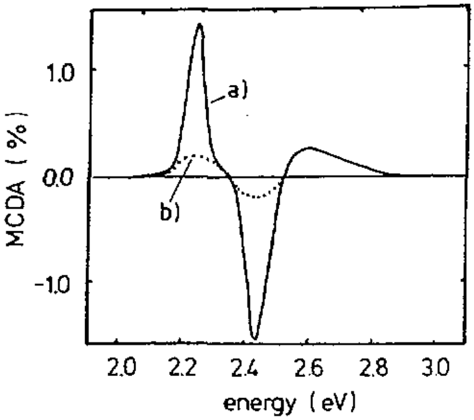

Figure 1. Curve (*a*): magnetic circular dichroism of the absorption (MCDA) of KCl:Tl irradiated with x-rays at 300 K for 30 min. The spectrum consists of a superposition of the MCDA of F centres and $Tl^0(1)$ centres. $B = 1$ T, $T = 1.4$ K. Curve (b) (dots): optical excitation spectrum of the Tl NMR signal.

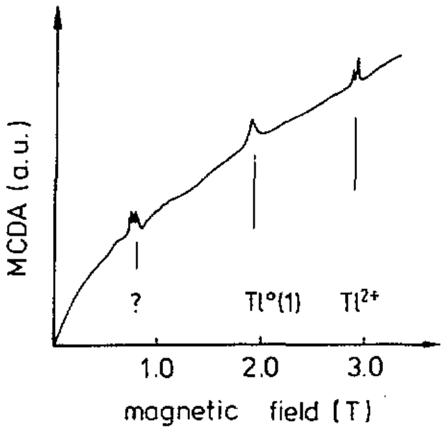

Figure 2. Magnetic field dependence of the MCDA of optically pumped F centres in KCl:Tl measured at 2.25 eV under optical pumping conditions (T = 1.4 K, $B_0 \parallel [100]$). The lines are cross relaxation signals due to $Tl^0(1)$ and Tl^{2+} centres and due to an unknown defect (see text).

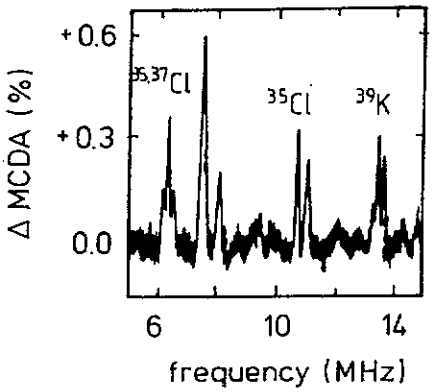

Figure 3. ODENDOR spectrum of the first-shell ^{39}K and second-shell ^{35}Cl and ^{37}Cl ligands of F centres in KCl:Tl measured as RF-induced increase of the optically pumped F centre MCDA for $B = 1.82$ T, $B \parallel [001]$.

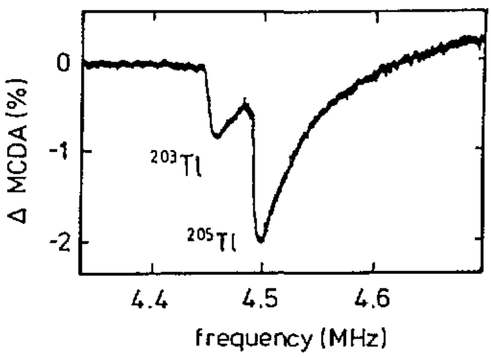

Figure 4. ^{203}Tl and ^{205}Tl NMR lines measured as RF induced decrease of the MCDA of F centres in KCl doped with Tl measured under optical pumping conditions at 2.25 eV at 1.4 K. The NMR frequencies correspond to the ^{203}Tl and ^{205}Tl Larmor frequencies for $B = 1.82$ T, $B \parallel [001]$.

NMR signals at half maximum has been measured to be about 150 kHz. Field shift measurements showed that the signals are indeed due to ^{203}Tl and ^{205}Tl nuclei.

The F centre ligand signals and the thallium signals increased with increasing RF power and were observable at any magnetic field value used in the experiments (1 to 5 T). This shows that these NMR signals are independent of the cross relaxation effects between Tl^{2+} and $Tl^0(1)$ centres and the F centres described above. The fact that the observation of the thallium NMR is only connected with the MCDA of F centres and not with the MCDA of the $Tl^0(1)$ centre occuring in the same spectral range was demonstrated by changing the optical wavelength through the MCDA of the F centre (figure 1, curve (b)). The spectral dependence of the MCDA, in which the Tl NMR lines could be observed, coincided precisely with that of the MCDA of the F centre.

With increasing light intensity for the MCDA measurements an increase of the Tl NMR signal amplitudes was observed while the MCDA intensity itself decreased. The rise time of the NMR signal after switching on the RF changed from 40 to 20 s upon increase of the light intensity by a factor of three. Similarly, the decay time after switching off the RF decreased from 400 to 200 s. These findings show that the observation of the Tl NMR is strongly related to the optical pumping of the F centres.

Thallium NMR signals were also observed in the MCDA of F centres in RbCl:Tl crystals which were irradiated with x-rays at 300 K to produce F centres. In this case the decay time of the Tl NMR was shorter (about 100 s) compared to that in the KCl crystals investigated under the same experimental conditions.

The Tl NMR was also investigated in x-ray-irradiated KCl crystals doped simultaneously with Tl and Ag, both at the same level of 0.5% in the melt. The presence of a high concentration of silver impurities was verified by measuring the EPR of paramagnetic Ag^0-related radiation centres (Ahlers 1988). However, no Ag NMR was detected in the MCDA of the optically pumped F centres up to 5 T, for which field the Larmor frequencies of ^{103}Ag and ^{105}Ag isotopes are in a frequency range where F centre ligand effects have been observed. The F centre ligand ENDOR and the Tl NMR signals were the same in the KCl:Ag,Tl as in the KCl:Tl crystals.

The experiments show that the observed effects of F centre ligand ENDOR and Tl NMR are connected with the optical pumping of the F centres which produces a non-equilibrium F centre electron spin polarization. This polarization is coupled to that of surrounding nuclei. It is known that a coupling due to hyperfine (HF) interactions can produce a polarization of the coupled nuclei (Abragam 1961).

RF-induced NMR transitions between nuclear magnetic Zeeman levels of neighbouring HF-coupled nuclei are detected here in a similar way to that used in conventional stationary ENDOR (Seidel 1961), only the role of the saturating microwave-induced EPR transitions is fulfilled here by the optical pumping of the F centre. The ENDOR effect is enhanced by the nuclear polarization of the neighbours produced by the HF coupling.

The understanding of the observation of the Tl NMR is less straightforward since the Tl nuclei do not normally belong to the surrounding lattice of the F centre.

Tl^+ cannot be the nearest neighbour of the F centre electron since this configuration is known to form $Tl^0(1)$ centres where the paramagnetic electron is mainly in a Tl^0 6p orbital adjacent to the Cl^- vacancy (Ahlers 1983).

The contact HF interaction prevails at short separation between the nuclei and the unpaired F centre electron while for larger distances the dipole–dipole interaction becomes dominant (Seidel 1961). The dipole–dipole interaction between Tl^+ and the F centre is calculated for a distance between Tl^+ and the F centre of five nearest-neighbour spacings d (d = 3.14 Å) to be 24 kHz, while for $4d$ it is 46 kHz and for $3d$ it is 110 kHz. For the latter distance (Tl^+ in shell 9) the contact term is practically zero (Kersten 1968).

From the linewidth of the Tl NMR signals, assuming that it is caused by the HF interaction, the dipole–dipole interaction is estimated to be at most of the order of 100–200 kHz, which would correspond to a distance of around three nearest-neighbour spacings between Tl^+ and the F centre.

As was shown by Bagraev *et al* (1977) the signs of the induced nuclear polarizations are different for the contact and dipole–dipole interactions. This would explain why the ligand ENDOR lines of the F centre change the MCDA intensity in the opposite direction to the Tl NMR transitions.

The question arises of whether a purely statistical model can explain the observation of the Tl NMR. Assuming an incorporation of 0.5% Tl into the crystal, the statistical chance of finding one Tl^+ substituting for K^+ within the vicinity of an F centre is about 100% for a cube extending to three nearest-neighbour distances along the three ⟨100⟩-directions. The largest separation between Tl^+ and the F centre would then be about $5d$.

For such a high concentration of Tl^+ a statistical model would be compatible with a HF interaction for Tl^+ which is likely to explain the observations, although we cannot say quantitatively how large the interaction must be, nor can we say how many of the doped Tl^+ we would see. However, atomic absorption spectroscopy measurements have shown that only about 10% of the Tl^+ doped in the melt is incorporated into the crystal (Ahlers 1985). Therefore, a purely statistical model is not likely to explain the observed effects.

Probably the Tl NMR is not only seen as that of a (distant) 'ligand' of the F centre with the same mechanism as assumed for the near neighbours. Maybe there are also cross relaxation effects between the Tl nuclear Zeeman levels and those of the F centre ligands analogous to those that led to the observation of the $Tl^0(1)$ and Tl^{2+} EPR lines in the MCDA of the optically pumped F centre. It seems that the assumption of a statistical distribution of Tl is not adequate to account for the rather strong signals. Although we cannot prove this, it is probable that the F centres are created by the x-ray irradiation in a spatial correlation with the Tl^+ impurities, such that they remain separated by a few lattice constants from the F centres, but close enough to 'communicate' via dipole–dipole interaction more strongly than would be expected from the purely statistical estimate. Such a spatial correlation with a rather large separation of several lattice constants was shown to exist between F centres and Eu^{2+} in BaFBr:Eu^{2+} on the basis of a quantitative analysis of cross relaxation effects measured with the MCDA technique Koschnick *et al* 1991).

The failure to observe the NMR of Ag nuclei may be explained by the nuclear magnetic moments of both ^{107}Ag and ^{109}Ag isotopes, which are an order of magnitude smaller than those of the two Tl isotopes. Apparently, neither the induced nuclear spin polarization nor cross relaxation effects are large enough to observe their NMR.

In principle the occurrence of a spatial correlation between F centres and Tl^+ could be checked by conventional ENDOR measurements, provided the separation between F centres and Tl^+ remains below four nearest-neighbour distances for which the dipole–dipole interaction should be resolvable. However, the number of F centres that can be produced by x-irradiation is too small for such experiments. Optical detection of ENDOR would be sufficiently sensitive, but according to our experience distant shells are not resolved (Söthe 1990).

4. Conclusions

We observed ENDOR of the first and second shells of ligands of F centres without microwaves in the MCDA of F centres under optical pumping conditions. The F centres were created by room temperature x-ray irradiation. A new effect, the detection of Tl impurity NMR at the Tl Larmor frequency, has been found, by monitoring the MCDA of the optically pumped F centres in Tl-doped KCl and RbCl. The NMR observations are explained by the hyperfine coupling between the F centres and the surrounding nuclei. It is assumed that the F centres are generated by the x-rays with a spatial correlation with the Tl^{+} impurities.

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