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H_2^- centres in NaF:H⁻

A V Egranov

Vinogradov Institute of Geochemistry, Academy of Sciences, Siberian Branch, Favorskii Street 1A, PO Box 4019, 664033 Irkutsk, Russia

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Abstract. The H_2^- centre in NaF is studied by electron spin resonance (ESR). The ESR spectrum shows a triplet due to the hyperfine interaction of an unpaired electron with the two equivalent protons. Each line of the triplet is further split owing to the superhyperfine interactions with the neighbouring nuclei of the first two shells (as in the case of the F centre) and the centre may also be described as being a neutral H_2 molecule embedded in an F centre.

1. Introduction

In alkali halides doped with OH^- or H^- ions, UV bleaching or x-ray irradiation at low temperatures leads to the formation of interstitial hydrogen atoms. Above LNT the interstitial hydrogen atoms start to diffuse and can be trapped at impurity defects to form molecular ion centres. Thus in KCl and KBr crystals the interaction with OH^- ions leads to the formation of H_2O^- centres [1, 2]; in SH^- -doped KCl, H_2S^- centres are created [3, 4]. In KCl crystals containing a mixture of OH^- and CN^- impurities, HCN^- centres are formed after thermal destruction of the H_3^0 centres [3], which are produced by the optical bleaching of OH^- centres at low temperatures.

In our previous paper [5] we have shown that, after x-ray irradiation of LiF:H⁻ crystals, H_2^- centres are created by the interaction of mobile interstitial hydrogen atoms with U centres. The H_2^- -centre ESR spectrum shows three broad lines which are due to the hyperfine (HF) interaction of an unpaired electron with the two protons. Each line has a further resolved structure for $B||\{111\}$ which arises (as in the case of the F centre) from the superhyperfine (SHF) interaction with the first two nuclear shells. The centre may be described as an F centre with an embedded hydrogen molecule: an $F(H_2)$ centre. This paper reports the results of electron spin resonance (ESR) measurements of these centres in NaF:H⁻ crystals.

2. Experimental details

The experimental technique and the preparation of the crystals have been described elsewhere [5, 6]. The U-centre concentration, as determined from IR optical absorption measurements, ranged from 10^{17} to 10^{18} cm⁻³. In contrast with LiF:H⁻, NaF:H⁻ contained a small amount of OH^- ions.

3. Experimental results and discussion

Figure 1 shows the ESR spectrum of H_2^- centres obtained after vacuum-UV irradiation of H^- -doped NaF for 30 min with a hydrogen lamp with a MgF_2 window at room temperature. It contains the three broad lines with intensity ratios 1:2:1 and with HF constant $a_p = (209 \pm 0.5) \times 10^{-4}$ T at RT. The spectrum is explained in a similar way to the case of lithium fluoride crystals [5] by a large splitting into three groups of lines due to HF interaction with two equivalent hydrogen nuclei ($I = \frac{1}{2}$), each of which is further split owing to SHF interactions with the neighbouring nuclei of the first two shells similar to those of the F centres. These centres can also be produced by x-irradiation.

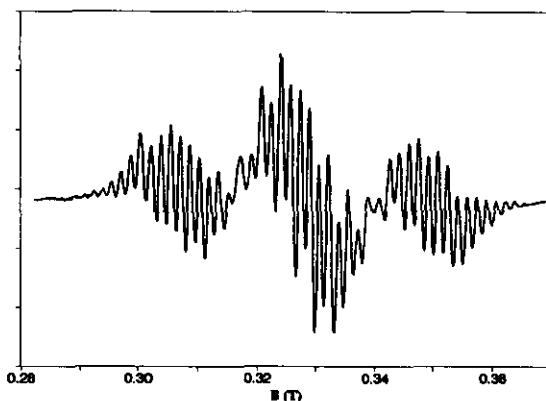


Figure 1. ESR spectrum of H_2^- centres in NaF:H⁻ $B_0 \parallel (110)$; $T = 77$ K; $\nu = 9239.3$ MHz. The 'pulsation' of the central group of lines is due to the presence of the F centres.

It should be noted that no saturation of the H_2^- -centre paramagnetic resonance absorption was found (as in the case of this centre in LiF). However, the observation of the H_2^- -centre resonance in NaF is hindered by the presence of the paramagnetic F centre, even with several milliwatts of microwave power, so that the lines decrease in amplitude from the centre of resonance non-uniformly (see figure 1).

The SHF structure of H_2^- centres in NaF is independent of the crystal orientation in the external magnetic field, indicating that the anisotropic constants are small. Similar behaviour of the SHF structure was observed for F centres in NaF [8] for which the first- and second-shell isotropic constants are almost equal and are close to the splitting between lines (for F centres in NaF the splitting is 37.7×10^{-4} T [8] and for H_2^- centres it is 15.5×10^{-4} T at RT). It may be proposed that in our case the SHF structure arises also from the interaction with the nuclei of two shells and its isotropic constants are almost equal.

The characteristic parameters of the ESR spectrum of the H_2^- centres in NaF are presented in table 1 together with the corresponding data for these centres in LiF crystals. The second-order HF-corrected g -value and A_p were obtained from the expressions described in [5, 7]. The values of g -factor are given without the second-order correction due to the SHF interaction; this leads to a smaller g -factor. Assuming that for H_2^- centres in NaF the first- and second-shell isotropic constants

are almost equal and are close to the splitting between lines, we may estimate the second-order SHF-corrected g -factor. The SHF correction gave a Δg value of about -5×10^{-4} and the g -factor is smaller than that of the free electron.

Table 1. The proton HF constants a_p and A_p , the g -factors and the splittings between the lines of the H_2^- centres in LiF and NaF.

	g -factor	a_p (10^{-4} T)	A_p (MHz)	Splitting (10^{-4} T)	T (K)
NaF	2.0021 ± 0.0003	209 ± 0.5	586 ± 1	15.5 ± 0.5	295
NaF	2.0021 ± 0.0003	211 ± 0.5	592 ± 1	16.5 ± 0.5	77
LiF	2.0023 ± 0.0003	230.5 ± 0.5	646 ± 2		295
LiF	2.0023 ± 0.0003	233.5 ± 0.5	654 ± 2		77

H_2^- centres in NaF and LiF crystals (table 1) show a small increase in the HF and SHF splittings with decreasing temperature to 77 K; the HF splittings increase by about 1–1.5% and the average increase in the SHF splitting is about 2–3% in LiF and somewhat higher in NaF (see table 1). This temperature dependence contrasts with that of the isotropic constants of the F centres (at least for the first two shells) which increase as the temperature is raised [8].

After vacuum-UV irradiation of NaF:H⁻ at 295 K, the optical absorption spectrum consists of only the F band. No absorption which may be associated with H_2^- centres was found. However, optical bleaching at RT as well as at LNT with the light from the F-centre absorption region leads to the disappearance of the H_2^- -centre ESR signal. It is possible that H_2^- absorption in NaF:H⁻ is the perturbed F band (as in the case of LiF:H⁻ [5]) and is obscured by the normal F absorption band. H_2^- centres in NaF are unstable at room temperature; their half-life is of the order of 10–12 h.

The g -factor and the HF interactions of the H_2^- centres in LiF and NaF crystals are isotropic at 295 K as well as at 77 K. This indicates that the molecule ion is freely rotating so rapidly that motional averaging is observed in ESR. In the rotating- H_2^- model the para states (with $I = 0$) and ortho states (with $I = 1$) are separated by an energy barrier (in the case of neutral H_2 , 120 cm^{-1}). This should result in a dominant singlet line at low temperatures and a HF triplet, enhanced at the expense of the singlet, at higher temperatures.

As mentioned above, the H_2^- centre may be described as being a neutral H_2 molecule embedded in an F centre. For H_2 in the free state, the relative concentrations of ortho and para modifications at various temperatures and the conversion rate between these states are well known. In the solid state, H_2 exhibits free rotation even at very low temperatures [10].

Since at high temperatures the hydrogen molecular mixture contains 75% of ortho and 25% of para molecules, the H_2^- -centre ESR spectrum shows a HF triplet with intensity ratios 1:2:1 (as if it originated from the two equivalent protons of the static molecule). At LNT the relative concentration of the ortho molecules is 50% and one expects to observe in the ESR spectrum of the H_2^- centre the HF triplet with intensity ratios 1:4:1 owing to enhancement of the para states having a singlet in the spectrum.

However, when the temperature is lowered to 77 K, no changes in the intensity ratios of the triplet were found, even after storing the LiF sample with H_2^- centres at this temperature for 15 d (if the ortho-to-para transition in H_2^- is slow). This indicates that, because part of the extra electron is bound to the molecule, the distance between

two hydrogen atoms should be larger (and the energy separation between ortho and para states should be smaller) than the d -value of 0.74 \AA in neutral H_2 .

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