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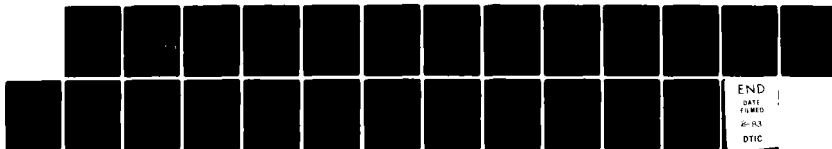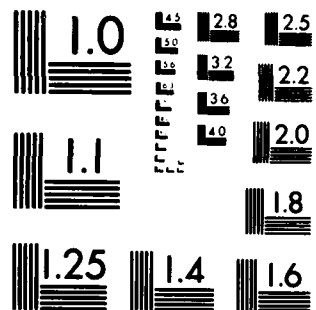   RESEARCH LAB SAN JOSE CA R T HARLEY ET AL. 21 DEC 82
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High Resolution Stark Spectroscopy of the

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by

R. T. Harley   and   R. M. Macfarlane

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HIGH RESOLUTION STARK SPECTROSCOPY
OF THE 6070A COLOUR CENTRE IN NaF
USING SPECTRAL HOLEBURNING

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ABSTRACT: The nature of the 6070A colour centre in NaF has been investigated using high resolution spectral holeburning. Well-resolved Stark splittings were observed in seven experimental geometries and it was found that the centre lacks inversion and has a plane of symmetry perpendicular to $(1\bar{1}0)$. The transition dipole is perpendicular to this symmetry plane and the difference of ground and excited state permanent dipole moments lies in this plane along $(1.000(5), 1.000(5), 1.445(10))$. The previous assignment of this line to an N_1 centre with C_{2h} symmetry is not consistent with these results. Possible alternative defect structures are considered.

INTRODUCTION

Spectral holeburning is a technique for very high resolution optical spectroscopy that can provide significant new information about the nature of defect centres in solids. It was recently found to be applicable to zero phonon lines of colour centre systems (Macfarlane and Shelby, 1979) and has the promise of being a general and powerful tool for their study. The technique exploits the fact that zero phonon lines are generally inhomogeneously broadened by more than 30 GHz, due to mechanisms such as random static strain, whereas the homogeneous width may be much less than 100 MHz. A single mode CW dye laser (linewidth ~1 MHz) is used to excite selectively a group of centres within the inhomogeneous profile and this produces in many cases a long-lived reduction of optical absorption, or hole, centred at the laser frequency. The width of the hole is usually of order 1 to 500 MHz and is determined by a combination of the homogeneous width, laser frequency jitter and other factors characteristic of the hole-burning mechanism. The increased resolution over conventional spectroscopy, typically a factor 10^3 or 10^4, makes possible the measurement of effects of external perturbations with great sensitivity.

Stark effect measurements have the advantage, for example over stress, that in addition to lowering the rotational symmetry, they are sensitive to the presence of inversion, i.e., a linear Stark effect denotes the absence of centre of symmetry and a quadratic effect implies the presence of inversion symmetry. In the conventional spectroscopy of colour centres, the Stark effect has never achieved its full potential as a probe of the symmetry of the centre because the splittings and shifts are usually less than the inhomogeneous linewidth and cannot be directly resolved. Thus it was necessary to resort to electric field modulation techniques (Kaplyanskii *et al.*, 1970; Kaplyanskii and Medvedev, 1971) and moment analysis (Johannson *et al.*, 1969) to deduce the Stark coefficients. This can be avoided by the use of

holeburning techniques since, as we show below, extremely well-resolved Stark splittings can be obtained with modest electric fields.

We have applied these ideas to a study of the colour centre in NaF whose zero phonon line is at 6069.65A ("the 6070A centre") This aggregate centre is readily produced by room temperature irradiation with, for example, x-rays, γ-rays or electrons and has one of the most prominent zero phonon lines in our samples of coloured NaF. It appears to have been first observed by Baumann (1967) and assigned by him on the basis of applied stress measurements, as an aggregate centre consisting of four fluorine vacancies in a (112) plane with four trapped electrons, a configuration which has C'_{2h} symmetry. This is the N_1 centre originally proposed by Pick (1960). As we shall see, this model is not consistent with the results of our Stark measurements. The zero phonon line of the N_1 centre had earlier been assigned by Johannsen *et al.* (1965, 1967) to the 5803A line and Kaplyanskii *et al.* (1969) found that this line had a quadratic Stark effect consistent with a C_{2h} symmetry, but did not study the 6070A centre. The 5803Å line was not detected in our samples.

Holeburning was recently reported to occur in the 6070A line (Levenson *et al.*, 1980) and polarization spectroscopy used to study the hole width as a function of temperature. The mechanism for burning the long-lived (>1 h) holes is not understood in any detail but, as in the case of the F_3^+ centre (Macfarlane and Shelby, 1979), it may involve loss of an electron from the centre by photoionization, or tunneling from an excited state. We have used holeburning to study the effect of external electric fields on this centre. We find a linear Stark splitting, i.e., the absence of a centre of inversion symmetry, in disagreement with the proposed C_{2h} model of an N_1 centre. More detailed analysis of the splittings for seven experimental geometries shows that the 6070A line is associated with an $A' \rightarrow A''$ transition at a centre of C_s symmetry, with a (110) reflection plane. The orientation of the vector

difference of ground and excited state permanent dipole moments has been determined to within 1° and lies in that plane, close to but not exactly along a $2\bar{2}3$ direction. The direction of the optical transition dipole (110) agrees with the proposal of Baumann (1967) and the polarization studies of Levenson *et al.* (1980), but the orientation of the centre and its lack of inversion are new results which could not have been obtained without the high resolution capability of holeburning spectroscopy.

EXPERIMENTAL

Single crystals of NaF from Optovac Incorporated were coloured by irradiation with a 2.5 Mrad ^{60}Co γ-ray source for 1 hr. After irradiation they were light pink due mainly to M-centre absorption. The measured absorption coefficient at the 6070Å zero phonon line was 7.0 cm^{-1}. Electric fields were applied along (100), (110) and (111) crystallographic axes. Samples ~1 mm thick for each of these geometries were prepared by cleaving in the case of (100) and by grinding and polishing in the case of (110) and (111). They were mounted in a Stark cell between stainless steel electrodes with a 0.1 mm mylar spacer to prevent injection of electrons. The cell was immersed in superfluid helium at 1.5K with optical access to the sample in directions perpendicular to the electric field.

Holes of width ~100 MHz were burnt in the 6070Å zero phonon line by resonant irradiation for 5 sec with 1 mW of light from a single mode CW dye laser (linewidth ~1 MHz) weakly focussed to a spot size of 500μ diameter within the sample. They were detected by attenuating the laser beam by a factor of 10^4 and monitoring the total red emission from the sample through a Corning 2-58 filter as the laser frequency was scanned over a frequency range ±5 GHz about the hole; the holes cause a reduction of emission intensity having a lifetime greater than 1 hr. The method of detection is equivalent to measurement of the absorption spectrum of the zero phonon line with ~100 MHz resolution.

Holes were burned in zero field and then a voltage was applied to the sample producing a splitting of the holes. Voltages of up to 10 kV were applied, although clearly resolved splittings could be observed for as little as 50 volts.

RESULTS

Examples of the hole spectra obtained for various experimental geometries are shown in Figs. 1 to 4, together with plots of the peak frequencies as a function of applied electric field. Table 1 gives details of each of the experimental geometries investigated. The enormous increase in information which these measurements provide over conventional Stark spectroscopy can be judged by reference to Fig. 5, which shows the conventional absorption spectrum of the 6070A line which has a 35 GHz inhomogeneous linewidth. Electric fields two orders of magnitude greater than those required to resolve all the Stark components in holeburning measurements (Figs. 1 to 4) must be applied before even poorly resolved splittings are observed.

In general, the observed pattern of splittings is a superposition of those for the assembly of centres which are structurally equivalent, but have different orientation with respect to the applied electric field. The observed splitting can therefore result from both removal of degeneracy of levels of a single centre (true Stark effect) and also from different linear shifts of singlet levels due to removal of orientational degeneracy alone (pseudo-Stark effect). The nature of the 6070Å centre may be deduced from the following considerations:

(i) The occurrence of linear electric field splittings demonstrates that the centre does not have inversion symmetry.

(ii) The spectra show an unshifted component only for the electric field (E_s) applied along (110) (see Fig. 3 and Table 1). This indicates that there is a subset of the centres for which the orientation of the permanent dipole moment is in the plane

perpendicular to the field direction, i.e., in a direction $(m,\overline{m},l)$, The shifted components in the spectra arise from other subsets of centres which have their permanent dipoles in planes such as (101) or (011) which are not perpendicular to the field.

(iii) The unshifted component is observed only for laser polarization parallel to E_S. Therefore the transition dipole is perpendicular to the permanent dipole, i.e., along (110).

(iv) The absence of unshifted components for $E_S//(100)$ and $E_S//(111)$ shows that no dipole moments lie along axes either of type $(m,n,0)$ with no restriction on m and n, or of type $(m,m,2m)$.

(v) From (i) to (iv) above, we conclude that the permanent dipole is directed along an axis of type (m,m,l) where $l \neq 0, 2m$ and that the corresponding transition oscillator is perpendicular to it, oriented along $(1\overline{1}0)$. The symmetry of such a centre in a cubic crystal is C_s with $(1\overline{1}0)$ symmetry plane. The orientation of the transition dipole perpendicular to the plane shows that the transition is between states transforming as A' and A''. The splittings observed thus arise purely from removal of the orientational degeneracy.

(vi) Table 1 and Fig. 6 give the predicted relative splittings and intensities for a cubic assembly of C_s centres. The splittings are proportional to the projections of the permanent dipoles onto the applied field whereas the intensities are given by the projections of the transition oscillators onto the direction of polarization of the laser (see Kaplyanskii and Medvedev, 1967, but note that the intensities which we calculate differ from those given in this reference). The number of components observed and their intensities are consistent with the type of centre specified in

(v) above. From the splittings observed for each direction of applied field, we obtain a value of ℓ/m; the average of these is $\ell/m = 1.445 \pm 0.010$. Furthermore, with this value of ℓ/m and from measurement of the width of the unshifted component observed for E_S, $E_L//110$ in an applied field of 64 kV/cm, we estimate that the permanent dipole is oriented within $\pm 0.2°$ of the $(1\bar{1}0)$ plane. An indication of the precision with which the orientation of the dipole is determined from these spectra is illustrated by the bars positioned above the spectra at fields of 5.51 and 4.55 kV/cm in Figs. 1b and 3a. In Fig. 1a, ($E_S//100$, $E_L//001$), the ratio of splittings is ℓ/m, whereas in Fig. 3a ($E_S//110$, $E_L//001$), the ratio is $\dfrac{(m+\ell)}{|m-\ell|}$. The bars show the positions expected for the case $\ell/m = 3/2$ and this is clearly inconsistent with the data. More careful analysis gives the value quoted above (see Table 1).

CONCLUSION

This analysis of the Stark splittings shows that the 6070A zero phonon line in coloured NaF originates from centres with C_s symmetry, the transition dipoles being perpendicular to (110) mirror planes with the difference between ground and excited state permanent dipoles in (1.000, 1.000, 1.445) directions and of magnitude 1.57 MHz/Vcm. It shows conclusively that the 6070A line does not originate from an N_1 aggregate centre of the type proposed by Pick (1960) and assigned to this line by Baumann (1967). It therefore does not contradict the suggestion by Johannson et al. (1967) that a line at 5303A may arise from the N_1 aggregate. That line shows no linear Stark effect up to 260 kV/cm as required for a centre of C_{2h} symmetry (Kapiyanskii et al., 1969). In addition, our observation of a linear Stark effect for the 6070A line shows that the suggestion by Baumann (1967) and Chandra and Holcomb (1969) that these two lines are due to transitions of the same centre is not correct.

The type of detailed information obtained here about the Stark coefficients, the orientation of the permanent dipole and the structure of the defect centre has not previously been obtainable from optical Stark effect studies and is an example of the kind of contribution that hole burning spectroscopy can make to our knowledge of such centres.

It is not yet possible to deduce the specific configuration of defects responsible for the 6070A centre. However, aggregates with sufficiently low symmetry are obtained when an M-centre is perturbed by a neighbouring F-centre, cation vacancy or impurity. It is interesting that the production of the 6070A and 5803A centres by irradiation of NaF are often mutually exclusive (e.g., this work, Johannson *et al.*, 1967; Kapiyanskii *et al.*, 1967), suggesting that the former may be an aggregate involving some impurity which traps F-centres and inhibits formation of the intrinsic N_1 centre of Pick.

TABLE 1

Splitting factors, s in MHz/(Vcm^{-1}) and relative intensities (in brackets) of Stark components of the zero phonon line in γ-irradiated NaF at 6069.65A observed for various orientations of applied field E_S and laser polarization E_L, compared to theoretical relative splittings and intensities for an assembly of centres with effective permanent dipole along (m,m,l) and transition oscillator along (1$\bar{1}$0) type axes. Experimental intensities may only be compared within each row. The magnitude of the difference between ground and excited state permanent dipoles is 1.57 MHz/Vcm^{-1}.

E_S	E_L	Observed				ℓ/m	Theoretical			
100	s	1.082	0.743				ℓ		m	
	100		(1)						(3)	
	001	(1)	(1.2)			1.456	(4)		(4)	
110	s	1.392	1.172	0.259	<0.006		$\dfrac{m+\ell}{\sqrt{2}}$	$\dfrac{2m}{\sqrt{2}}$	$\dfrac{m-\ell}{\sqrt{2}}$	0
	110	(1.25)		(1)	(6.7)		(2)		(2)	(8)
	1$\bar{1}$0	(1)	(1.8)	(1.6)			(2)	(4)	(2)	
	001	(1)		(1.1)		1.432	(2)		(2)	
111	s	1.539	0.641	0.243			$\dfrac{2m+\ell}{\sqrt{3}}$	$\dfrac{\ell}{\sqrt{3}}$	$\dfrac{2m-\ell}{\sqrt{3}}$	0
	111		(1)					(3)		
	1$\bar{1}$0	(1.7)	(1.6)	(1)		1.446	(3)	(2)	(3)	

Average   1.445
          ±.010

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FIGURE CAPTIONS

Figure 1. Stark effect on the holeburning spectrum of the 6070A line in γ-ray coloured NaF for $E_S//(100)$. (a) $E_L//(100)$; (b) $E_L//(001)$. The bars above the 5.51 kV/cm trace show where the hole positions would be if $\ell/m=1.5$ (see Results section); (c) Hole positions as a function of applied electric field from which the splitting factors s in Table 1 were obtained.

Figure 2. Stark effect on the 6070A line of NaF for $E_S//(111)$. (a) $E_L//(111)$; (b) $E_L//(1\bar{1}0)$ (c) Hole positions as a function of applied electric field.

Figure 3. Stark effect on the 6070 line of NaF for $E_S//(110)$. (a) $E_L//(001)$. The bars above the 4.55 kV/cm trace indicate expected hole positions for the case $\ell/m=1.5$; (b) Hole positions as a function of applied electric field.

Figure 4. Stark effect on the 6070A line of NaF for $E_S//(110)$. (a) $E_L/(110)$; (b) $E_L//1\bar{1}0)$ (c) Hole positions as a function of applied electric field. The presence of an unshifted component in (a) shows that the permanent dipoles of one subset of centres lie in a plane $\perp$ to (110).

Figure 5. Conventional absorption spectrum of the 6070A centre in NaF. Trace (a) shows the convolution of the zero field inhomogeneous linewidth of 35 GHz and spectrometer width of 3 GHz. Trace (b) shows a barely resolved Stark splitting for $E_S=\pm 1.1$ kV/cm//(100) in unpolarized light. The bars show the expected splitting pattern.

Figure 6. Theoretical Stark splitting patterns for a centre of C_s symmetry and E_S and E_L in the directions shown. The numbers beside the bars are intensities in arbitrary units and the splittings are shown as a function of ℓ and m where the permanent electric dipole moment is in the direction (m, m, ℓ).
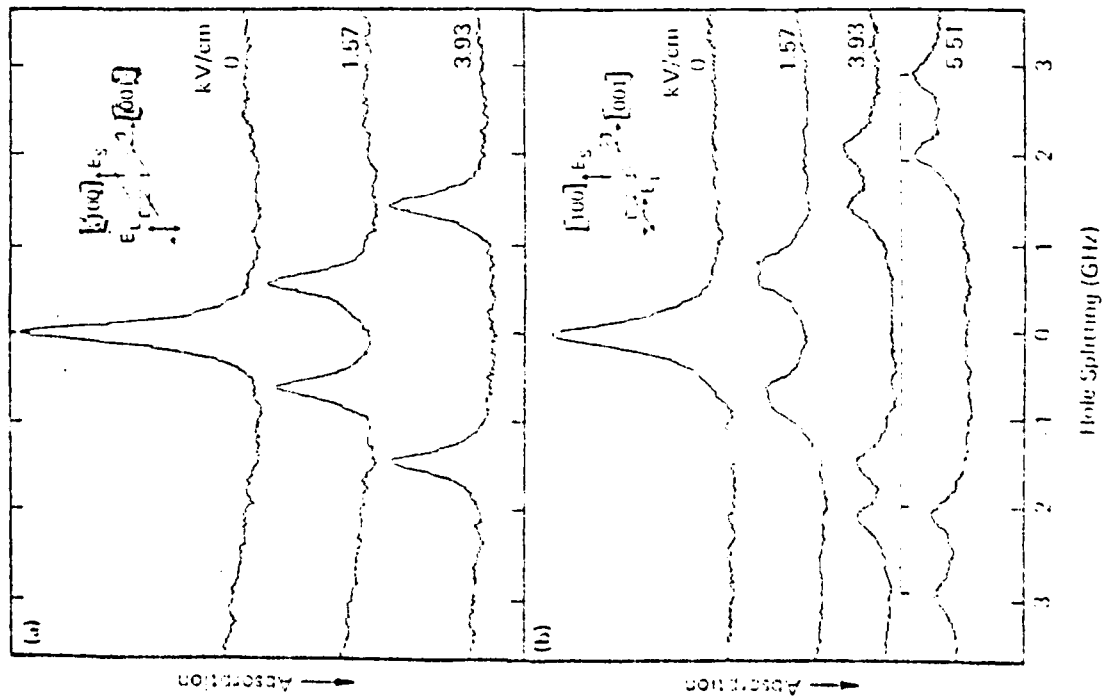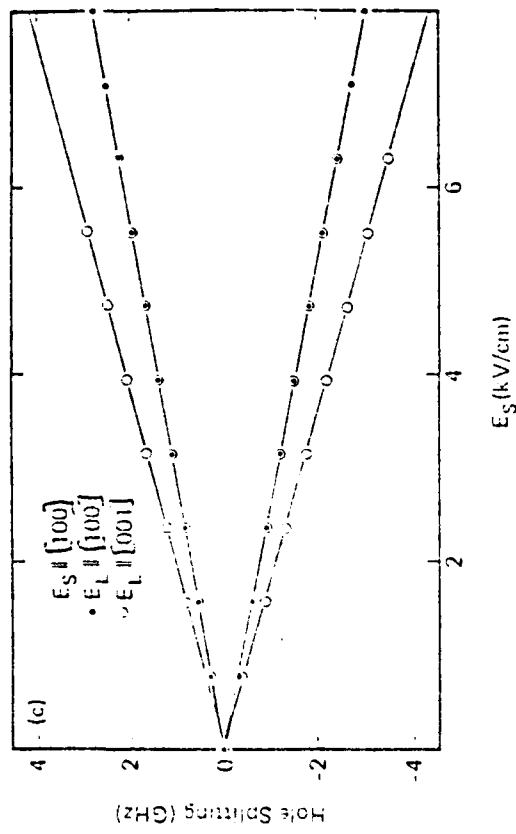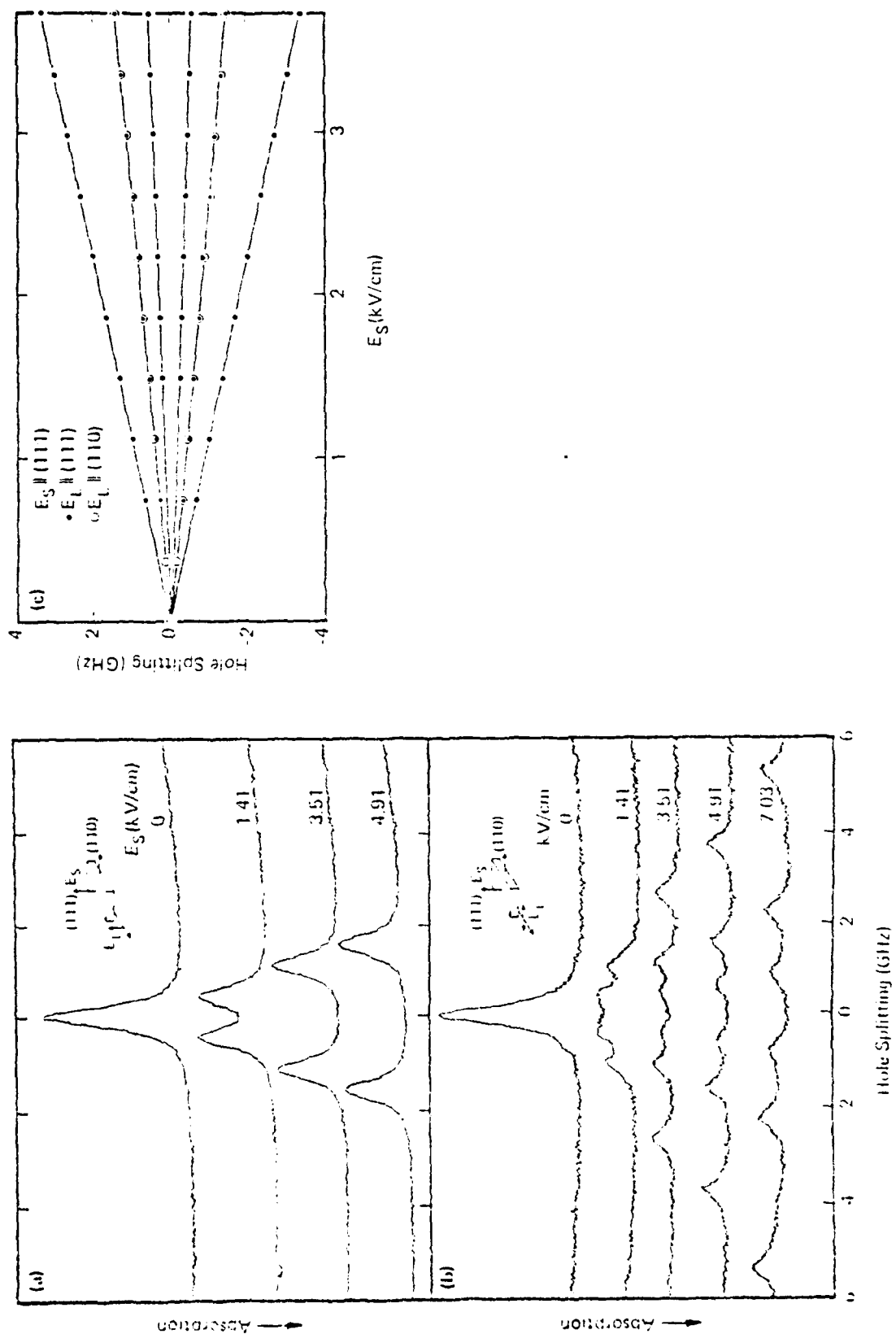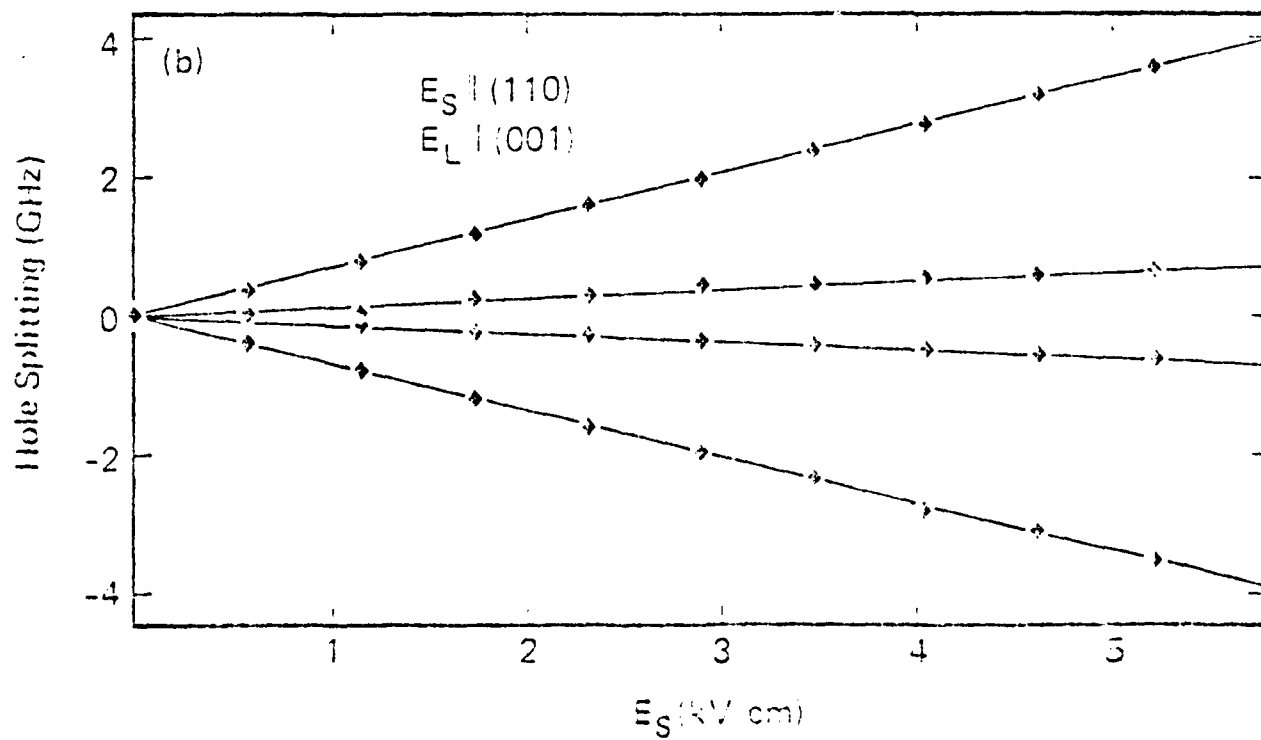
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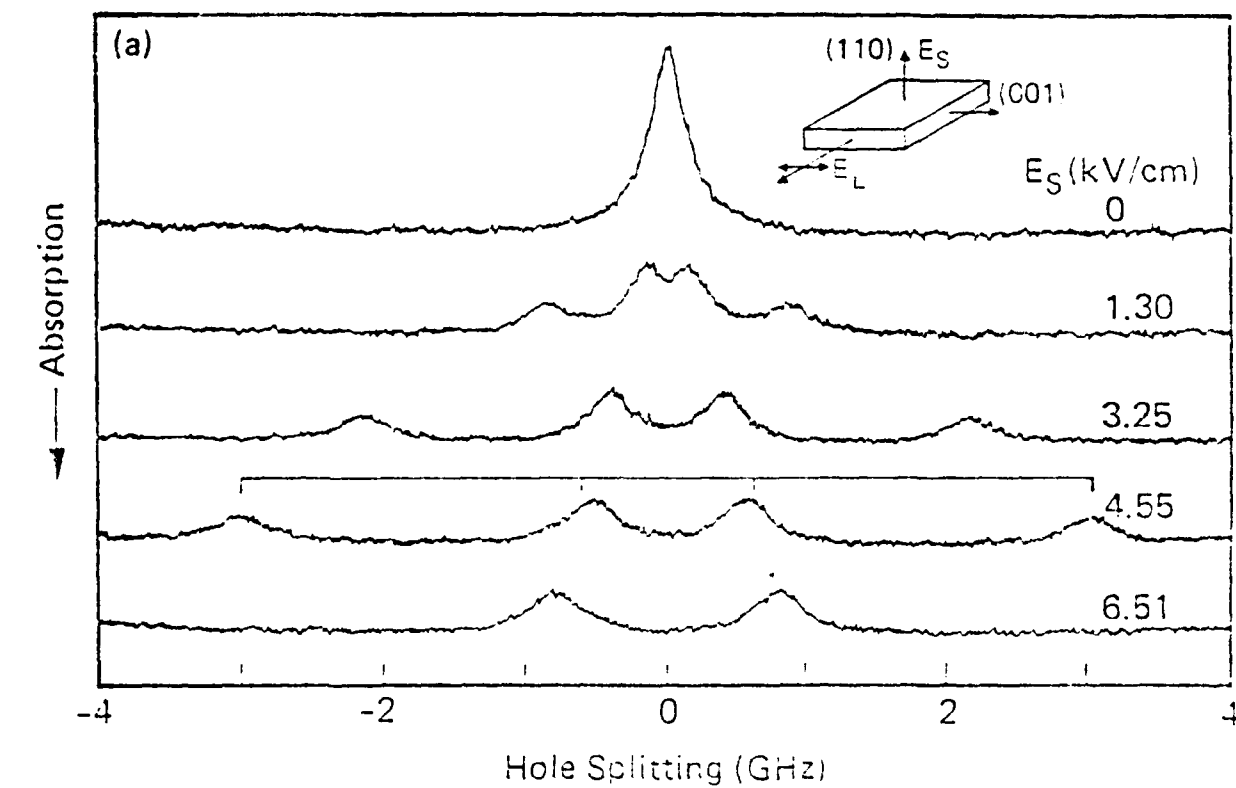
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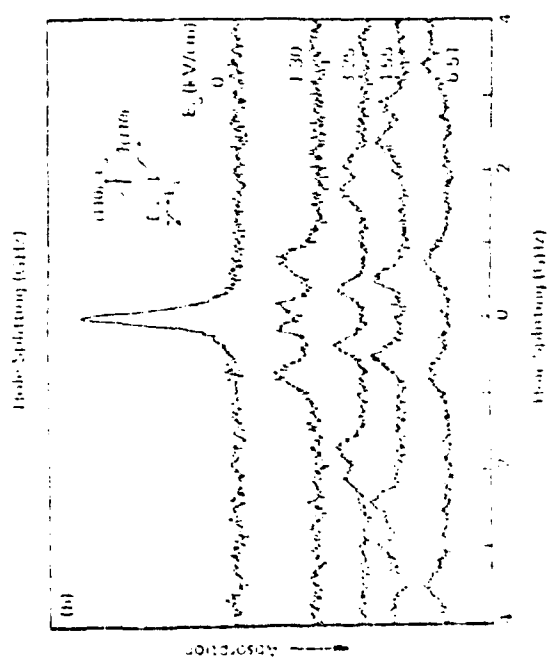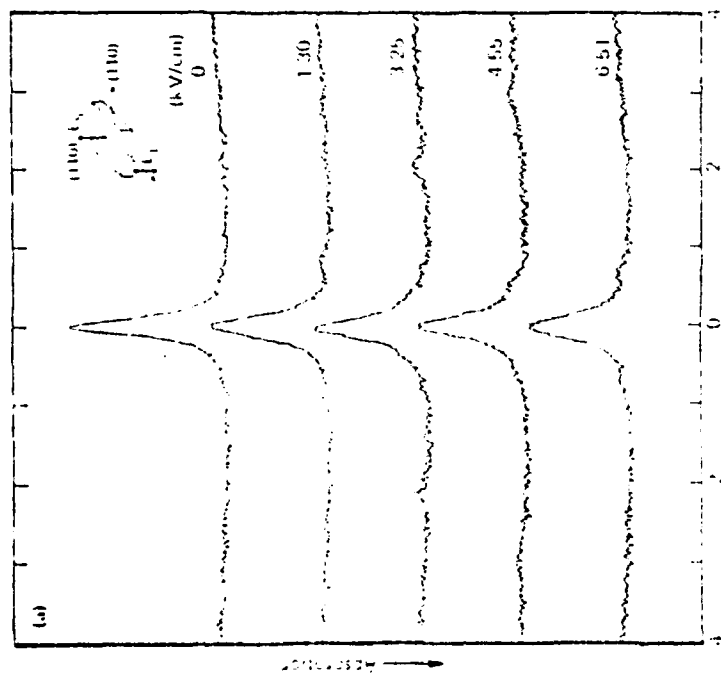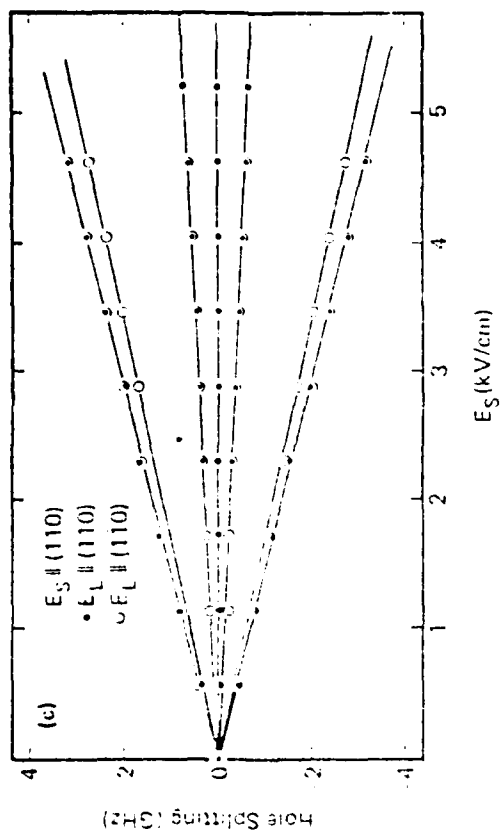
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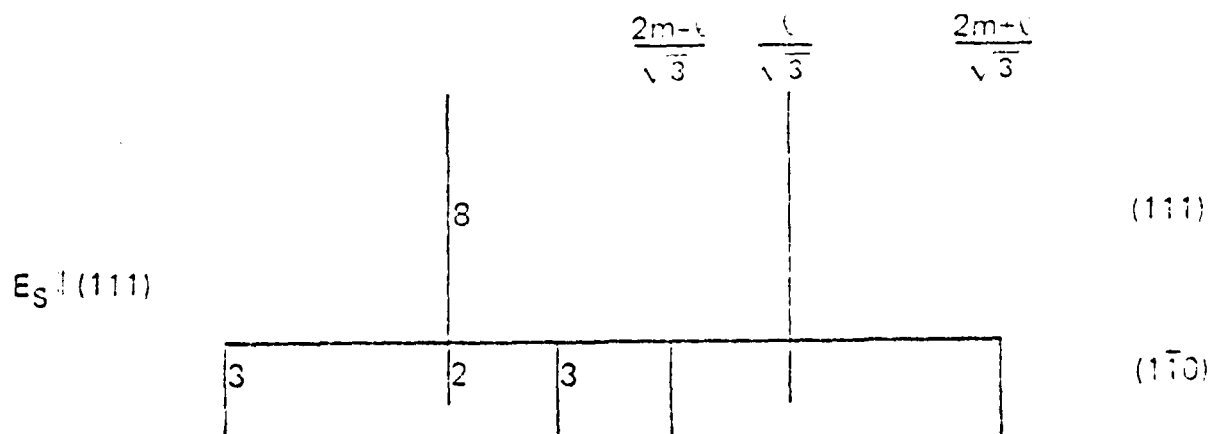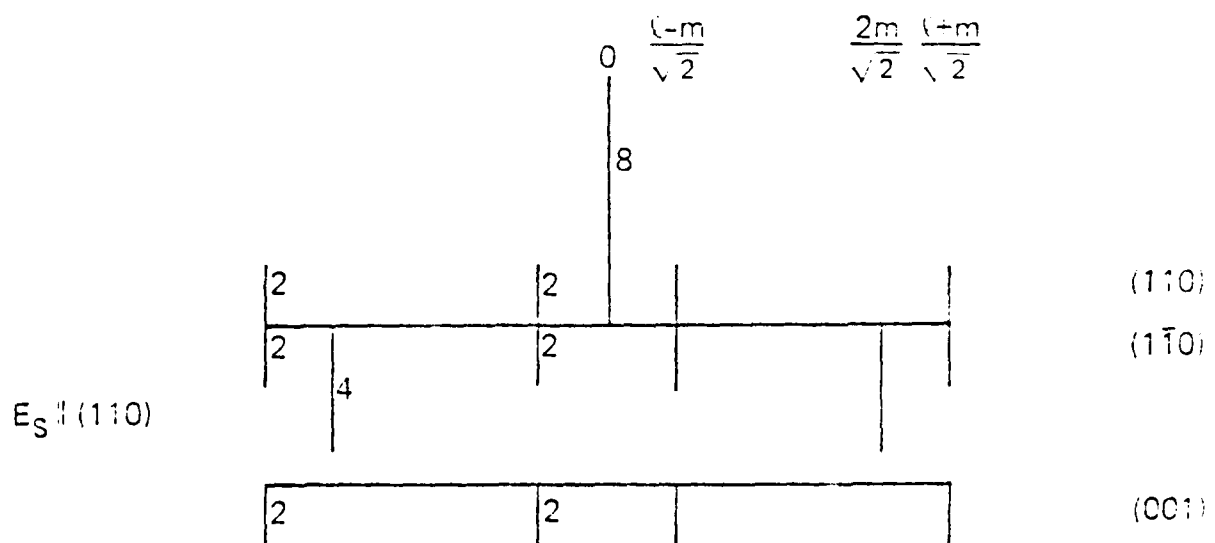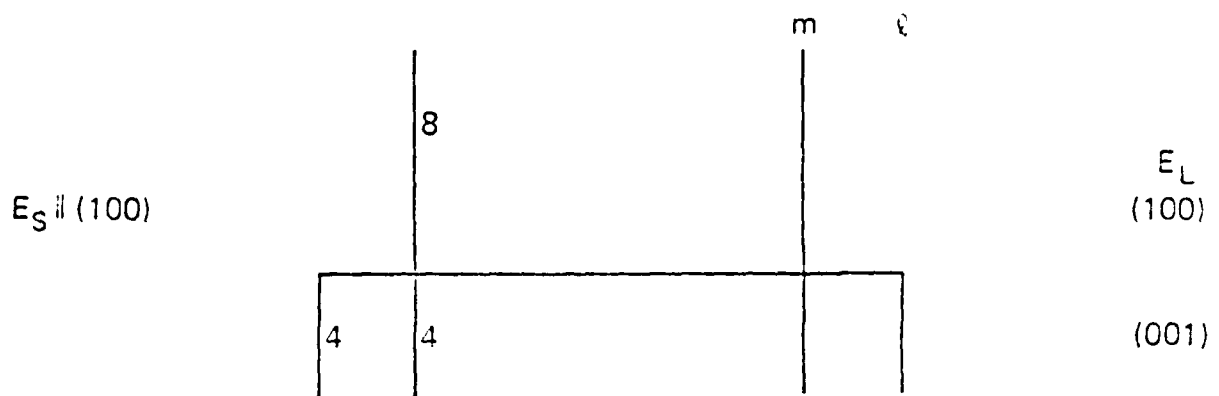
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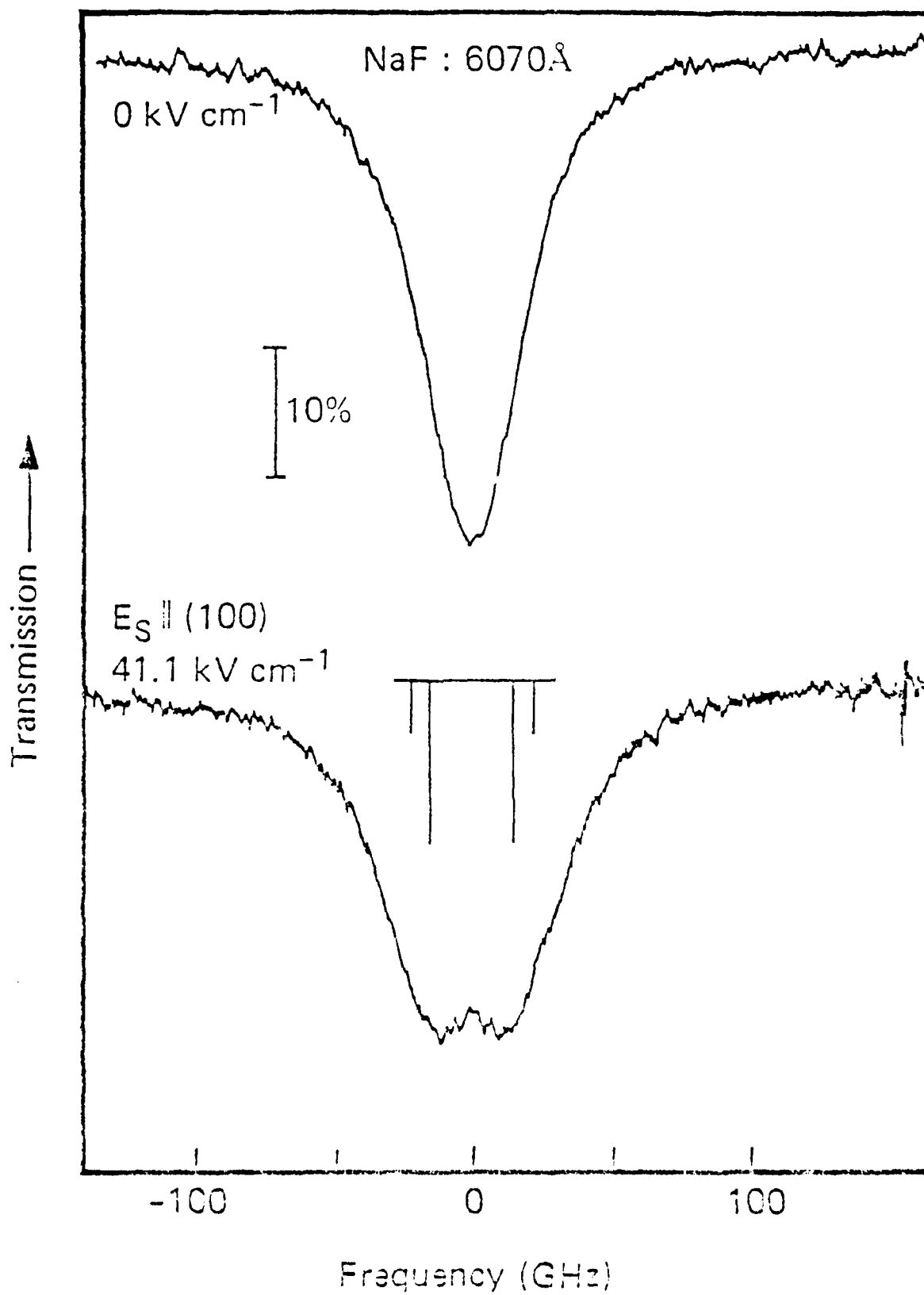
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