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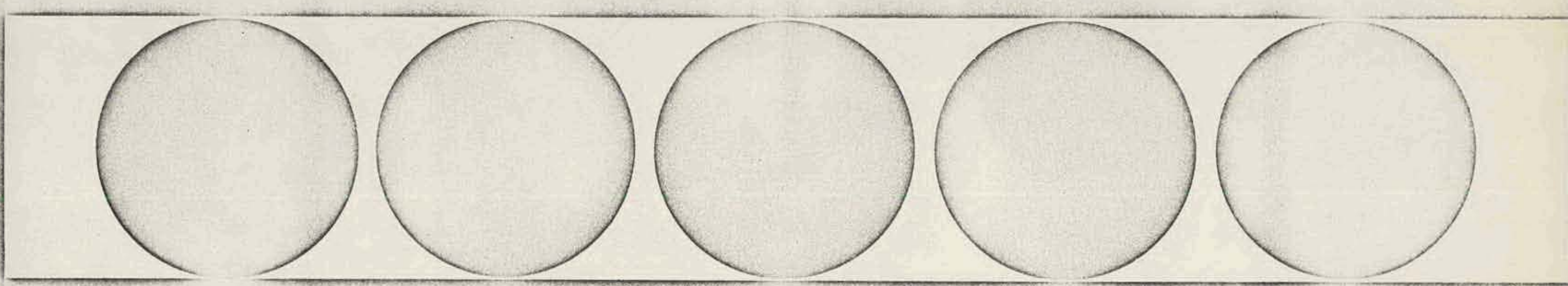

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PARAMAGNETIC RESONANCE SPECTRA OF THE $3d^5$ CONFIGURATION OF CHROMIUM IN ZnSe AND ZnTe

by

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ABSTRACT: Paramagnetic resonance measurements have been made for the $3d^5$ configuration of Cr^+ in ZnSe and ZnTe. The g factor, the cubic crystalline field parameter α, the hyperfine interaction with Cr^{53}, $A(Cr^{53})$ and the hyperfine interaction A_{Zn} with Zn^{67} nuclei occupying any of the twelve equivalent cation sites nearest the chromium have been determined. These resonance parameters are compared with those previously measured for Cr^+ in cubic ZnS and CdTe and the variations from crystal to crystal are found to be consistent with changes in the covalency of the bonds and with lattice distortions caused by incorporating Cr^+ substitutionally for the much smaller divalent zinc. The hyperfine interaction with Zn^{67} (or Cd^{111} and Cd^{113}) at second neighbor sites is, unlike the interaction of the isoelectronic Mn^{++} with these sites found to vary from crystal to crystal in a manner consistent with changes in the covalent bonding.

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INTRODUCTION

Chromium has previously been shown to act as an acceptor in II-VI compounds.[1, 2] Chromium enters the lattice substitutionally for the divalent cation. In this electrically neutral state, independent of whether the bonding is ionic or covalent or some mixture of both, the electronic charge centered on the chromium site can be designated by a 3 d^4 configuration. When chromium accepts an electron, paramagnetic resonance has shown both in the case of ZnS,[1] and CdTe[2] that the electron attaches itself to the chromium as a d electron and the chromium can in this state be designated by a 3 d^5 configuration. In this paper the observation by paramagnetic resonance of the 3 d^5 configuration of chromium in two other II-VI compounds of the zincblende structure, ZnSe and ZnTe is reported. Although the bonding in these compounds is a mixture of covalent and ionic bonding the 3 d^5 configuration of Cr will for the sake of brevity be designated by Cr^+. For Cr^+ in these compounds the g factor, the cubic field splitting parameter a, the hyperfine interaction $A(Cr^{53})$ with Cr^{53}, and the hyperfine interaction A_{Zn} with Zn^{67} (4% abundant) occupying second neighbor positions have been determined. A comparison of the variation of these parameters for Cr^+ in the four zincblende lattices for which they have been observed is made. The variations are consistent with changes expected on the basis of differences in the degree of covalent bonding in the various lattices and also of lattice distortions in incorporating Cr in the zinc compounds. In striking contrast to the isoelectronic Mn^{++} in these compounds the hyperfine interaction of Cr with second neighbor sites is found to vary from lattice to lattice in a manner consistent with variations in the degree of covalent bonding.

EXPERIMENTAL.

The crystals of ZnSe were grown by L. Suchow and J. Scardefield. These were grown from the melt either in an oven or by R. F. heating. Chromium was found to be invariably present as an impurity in concentrations of the order of one part in a million. The chromium is believed to have diffused in to the ZnSe from the graphite crucibles at the 1500°C temperature of the melt.

The crystals of ZnTe were grown by J. Kucza. They were grown from a melt containing 50% excess tellurium which has the effect of lowering the melting point. Chromium was added in metallic form.

The resonance measurements were carried out at 77°K. At this temperature some of the chromium centers were found to have a $3\,d^5$ configuration in both ZnSe and ZnTe. The number in this configuration could be increased some three fold by irradiating the crystal with light of energy near the band gap. When the light was removed the number of Cr^+ would remain undiminished over a period of hours indicating that the level due to Cr^+ is deep with respect to the conduction band. This effect of light of energy near the band gap is similar to that of Cr in ZnS.[1]

RESULTS

The Cr^+ resonance spectra in ZnSe and ZnTe are shown along with that in ZnS in Fig. 1. The spectra were taken with the magnetic field parallel to the [001] direction. The five fine structure transitions expected for the $^6S_{5/2}$ ground state of the $3d^5$ configuration have been indicated by the labels a to e. The separation of the fine structure lines depends on the cubic field parameter a and the orientation of the crystal with respect to the field.[3] The spectra in the [001] direction of Fig. 1 along with measurements in other directions have been used to determine a.

A hyperfine interaction with the 10% abundant isotope Cr^{53} is observed in each case. It is most clearly resolved in a direction where the five fine structure lines coincide. One such direction is in the (110) plane approximately 30° from the [001] direction. The spectrum in this direction is shown in Fig. 2 for ZnSe and the four hyperfine transitions due to Cr^{53}($I = 3/2$) are indicated by the arrows.

In Fig. 1 the structure on the $1/2 \rightarrow -1/2$ transition (labelled c in each case) is similar to the structure that has been observed for the $1/2 \rightarrow -1/2$ transition of Mn^{++} in ZnS,[4] CdS[5, 6] and CdTe[6] and of Cr in CdTe.[2] It is attributed to a virtually isotropic hyperfine coupling between the electrons in the $3d^5$ configuration and the magnetic nuclei Zn^{67} (or Cd^{111} and Cd^{113}) occupying any of the twelve equivalent cation sites nearest the impurity. The parameter describing this interaction is A_{Zn} (or A_{Cd}) and is equal to twice the spacing between the hyperfine lines.[5, 6] It is seen in Fig. 1 that A_{Zn} increases in going from ZnS to ZnSe to ZnTe.

The resonance parameters that have been measured for Cr^+ in ZnSe and ZnTe are given in Table 1 along with the previous measurements in ZnS[1] and CdTe[2].

DISCUSSION OF THE RESULTS

The g values

Watanabe[7] has shown that for the $^6S_{5/2}$ ground state of the $3d^5$ configuration the g value should be less than the free electron value 2.0023. This is seen to be the case for the four crystals in Table I with the g value in ZnTe being equal to 2.0023. The variation in the g values from crystal to crystal is attributed to the effects of covalent bonding. Fidone and Stevens[8] pointed out that the g value will depend on the degree of covalent bonding. Watanabe[9] has calculated that an increase in the amount of covalent bonding leads to an increase in the g value. The degree of covalent bonding increases as the anion is changed from sulfur to selenium to tellurium and a corresponding increase is seen in the g value for the three zinc compounds.

The g value for Cr^+ in ZnTe is seen to be significantly higher than in the cadmium compound of the same anion, CdTe. This is due to an effect which affects not only the g value but, as will be seen, the other resonance parameters as well. It is a result of a lattice distortion caused by incorporating Cr for the smaller zinc ion. The ionic radius of Cr^+ may be extrapolated from the sizes of the isoelectronic Mn^{++} (0.80 Å) and Fe^{+++} (0.64 Å) to be about 0.96 Å. The Zn^{++} ion has a radius of 0.74 Å whereas the Cd^{++} ion has a radius of 0.97 Å. Cr^+ should therefore substitute for Cd^{++} without any lattice distortion. However, its substitution for the much smaller Zn^{++} ion requires the lattice to undergo a local expansion to accommodate the chromium. The charge on the Cr^+ will therefore in the zinc compound lattice overlap more with the charge on the neighboring anions than in the cadmium compound. This implies that the chromium doped zinc compund is more covalent than the cadmium compound and accounts for the larger g value for Cr^+ in ZnTe than in CdTe. Lattice distortions due to size mismatch have been previously reported for Mn^{++} in II-VI compounds.[10]

The a values

The a value is a measure of the effect of the crystalline field at the Cr^+ site produced by the charge on the anions. The crystalline field should decrease as the separation of the anions and Cr^+ is increased. However, as seen in Table 1 the a value is seen to increase for the zinc compounds in going from smallest lattice, ZnS, to the largest, ZnTe. A similar result is found for Mn^{++} in these compounds[11] and is due to changes in the degree of covalent bonding. As the amount of covalent bonding increases the charge on the anions and on the cations is no longer concentrated at the lattice points but moves out into the intermediate region. The crystalline field produced by the charge on the anions at the cation site therefore increases because of the greater proximity of the charges. The increase in the a value in going from ZnS to ZnTe indicates that the covalency in the bonding is increasing at a rate more than fast enough to offset the increasing separation of the centers of the cationic and anionic charges as given in Table 1.

The value of a, 3.1×10^{-4} cm^{-1}, in CdTe is less than a in any of the three zinc compounds, particularly as compared to the value of a in ZnTe, 6.6×10^{-4} cm^{-1}. This cannot simply be accounted for by the larger cation-anion separation in CdTe as compared to ZnTe. The larger value can, however, arise due to lattice distortion caused by incorporating Cr^{+} at a Zn site. In the presence of distortion the charge on the Cr^{+} in the zinc compound will be in more intimate contact with the anionic charge. This results in a higher crystalline field and accounts for the larger a value measured in ZnTe than in CdTe.

The A(Cr^{53}) values

The hyperfine splitting characterized by A(Cr^{53}) is the result of a magnetic interaction between the nuclear magnetic moment of the 10% abundant Cr^{53} and the magnetic field produced at the Cr^{53} nucleus by the $3d^5$ electrons. This magnetic field results from a polarization of the inner paired s^2 electrons by the aligned spins of the $3d^5$ configuration.[12] The mechanism producing the field is a spin dependent exchange mechanism and will depend on the degree of overlap of the wave functions of the inner s^2 electrons and that of the $3d^5$ electrons. The degree of overlap will depend on the covalency in the bonding and would be expected to be less the more covalent the bond. This should result in lower A(Cr^{53}) values for the crystals with the more covalent bonds and is seen to be the case in Table 1. The more covalent ZnTe has a lower A(Cr^{53}) value than ZnS. In addition a comparison of ZnTe and CdTe shows the A(Cr^{53}) value in ZnTe to be lower. This is an indication of more covalent bonding in ZnTe caused by a lattice distortion in incorporating the larger Cr^{+} for Zn.

The A_{Zn} and A_{Cd} values

The A_{Zn} (or A_{Cd}) characterize an interaction between the nuclear magnetic moment of Zn^{67} (or Cd^{111} and Cd^{113}) occupying second neighbor sites and the magnetic field produced at these sites by the $3d^5$ configuration. Since the spins and moments of the Zn and Cd nuclei are known the $A_{Zn, Cd}$ values may be used to calculate the magnetic field $H_{Zn, Cd}$ produced by the Cr^{+} at the twelve nearest cation sites. The fields are given in Table II. Also included for comparison are the results that have been obtained for the interaction of the isoelectronic Mn^{++} with second neighbor sites in ZnS,[4] CdS,[5,6] and CdTe.[6] The magnetic field at the second neighbor sites is a measure of the contact of the $3d^5$ wave function with these sites.

The results for Mn^{++} as given in Table II indicate that the magnetic field at the second neighbor site is independent of lattice size, the covalency in the bonds and whether the cation is zinc or cadmium. For Cr^{+}, however, the magnetic fields at the second neighbor sites are much larger than for the isoelectronic Mn^{++} and there is a variation in $H_{Zn, Cd}$ from crystal to crystal. The magnetic field at the second neighbor sites increases as the covalency in the bonds increase from the sulphide to the tellurides. The smaller value for $H_{Zn, Cd}$ in CdTe than in ZnTe may be due to the larger size of CdTe or may possibly reflect lattice distortion in incorporating Cr^{+} for Zn.

The variation in the interaction of Cr^{+} with second neighbor sites as compared to the lack of variation for Mn^{++} is undoubtedly due to the greater extent of the Cr^{+} wave function as compared to Mn^{++}. This is to be expected since Cr in this configuration has accepted an electron. Mn^{++} on the other hand is electrically neutral.

In summary the resonance measurements that have been made of Cr^{+} in four zincblende lattices show that there are variations from crystal to crystal of the resonance parameters g, a, A(Cr^{53}) and $A_{Zn, Cd}$. The variations are consistent with changes in the degree of covalency in the bonds and with lattice distortions caused by incorporating the larger Cr^{+} in place of divalent zinc.

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Table I. The resonance parameters of Cr^+ in four zincblende lattices.

	Cation-Anion separation A	T °K	g	a	A(Cr^{53})	A_{Zn} or A_{Cd}
				10^{-4} cm^{-1}		
ZnS	2.35	77	1.9995 ± .0005	3.9 ±0.1	13.4 ± 0.1	1.23 ± 0.15
ZnSe	2.46	77	2.0016 ±.0005	5.35 ± 0.08	13.3 ± 0.2	1.81 ± 0.10
ZnTe	2.63	77	2.0023 ±.0005	6.60 ± 0.2	12.4 ± 0.2	3.59 ± 0.11
CdTe	2.81	4.2	1.9997 ±.0003	3.1 ± 0.6	12.781 ± 0.005	10.6

Table II. The interaction of Cr^{+} and $Mn^{++}(3d^{5})$ with magnetic nuclei at second neighbor sites in II-VI compounds.

			A_{Zn} or A_{Cd} 10^{-4} cm^{-1}	H_{Zn} or H_{Cd} oersteds
Cr^{+}	in	ZnS	1.23	3.46×10^{4}
		ZnSe	1.81	5.08×10^{4}
		ZnTe	3.59	10.1×10^{4}
		CdTe	10.6	8.4×10^{4}
Mn^{++}	in	ZnS	0.75	2.1×10^{4}
		CdS	2.6	2.1×10^{4}
		CdTe	2.6	2.1×10^{4}

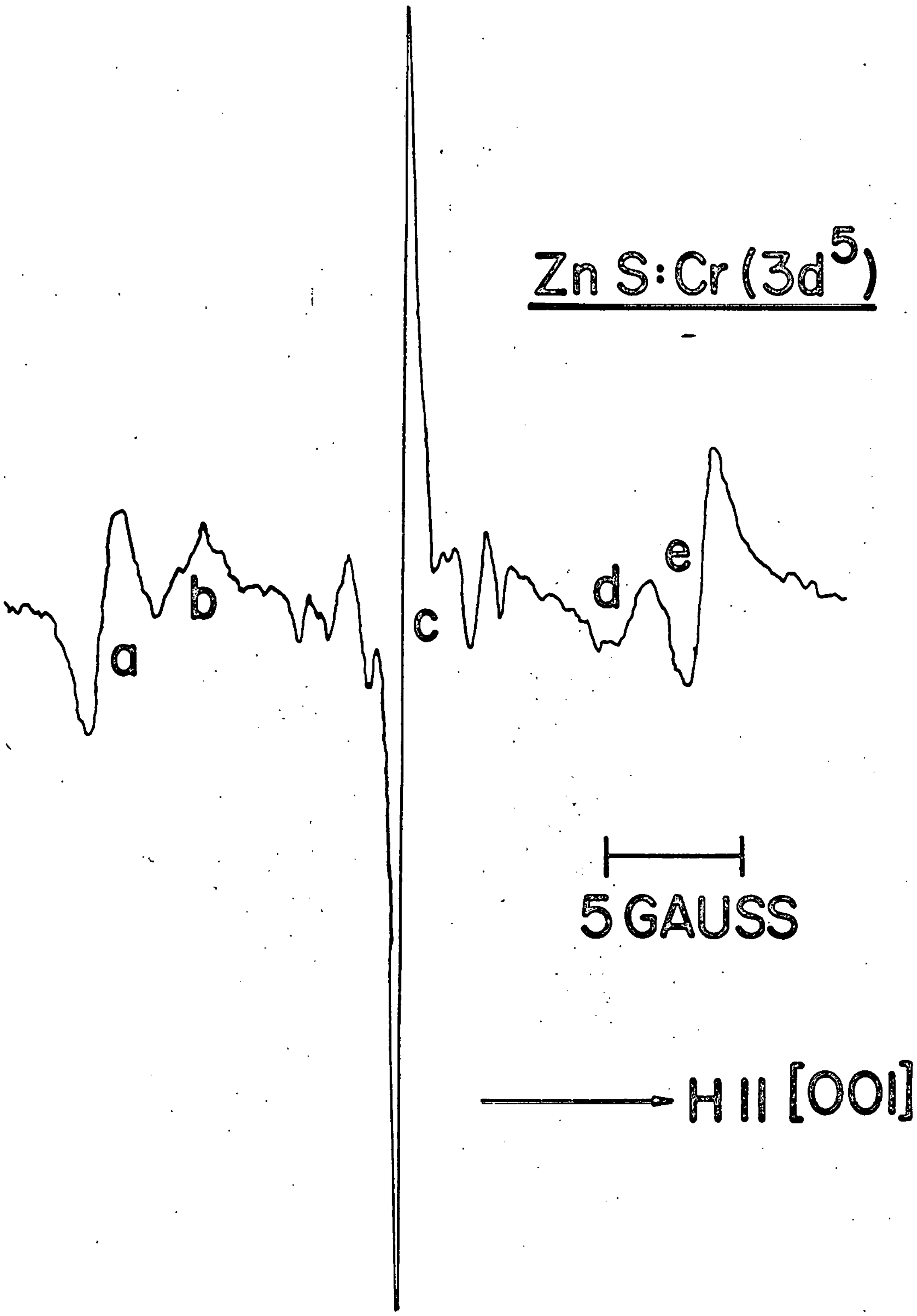

Figure 1a Paramagnetic resonance spectrum at 77°K of Cr^+ in ZnS.

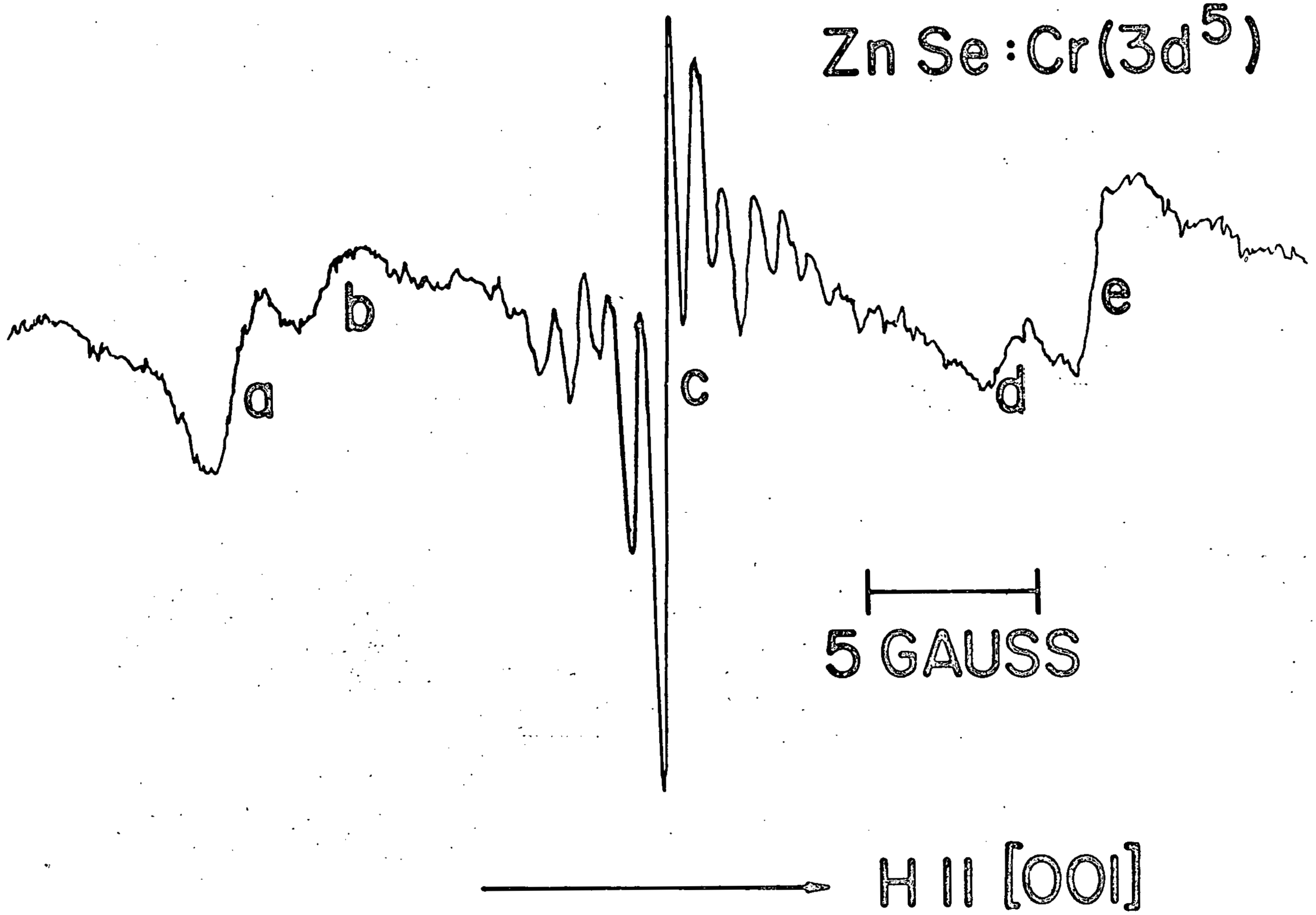

Figure 1b Paramagnetic resonance spectrum at 77°K of Cr$^+$ in ZnSe.

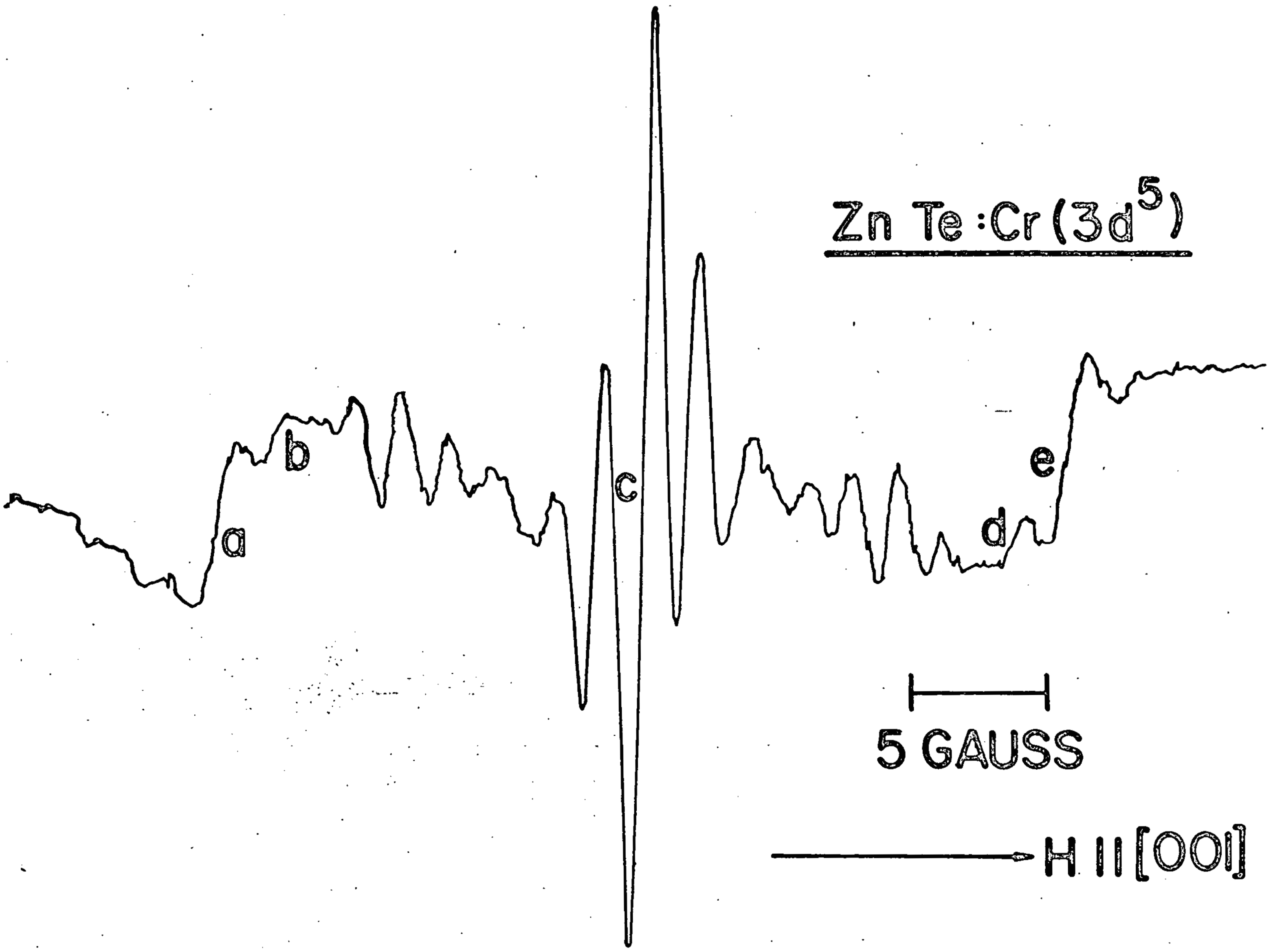

Figure 1c Paramagnetic resonance spectrum at 77°K of Cr^+ in ZnTe – taken with the magnetic field H parallel to the [001] direction.

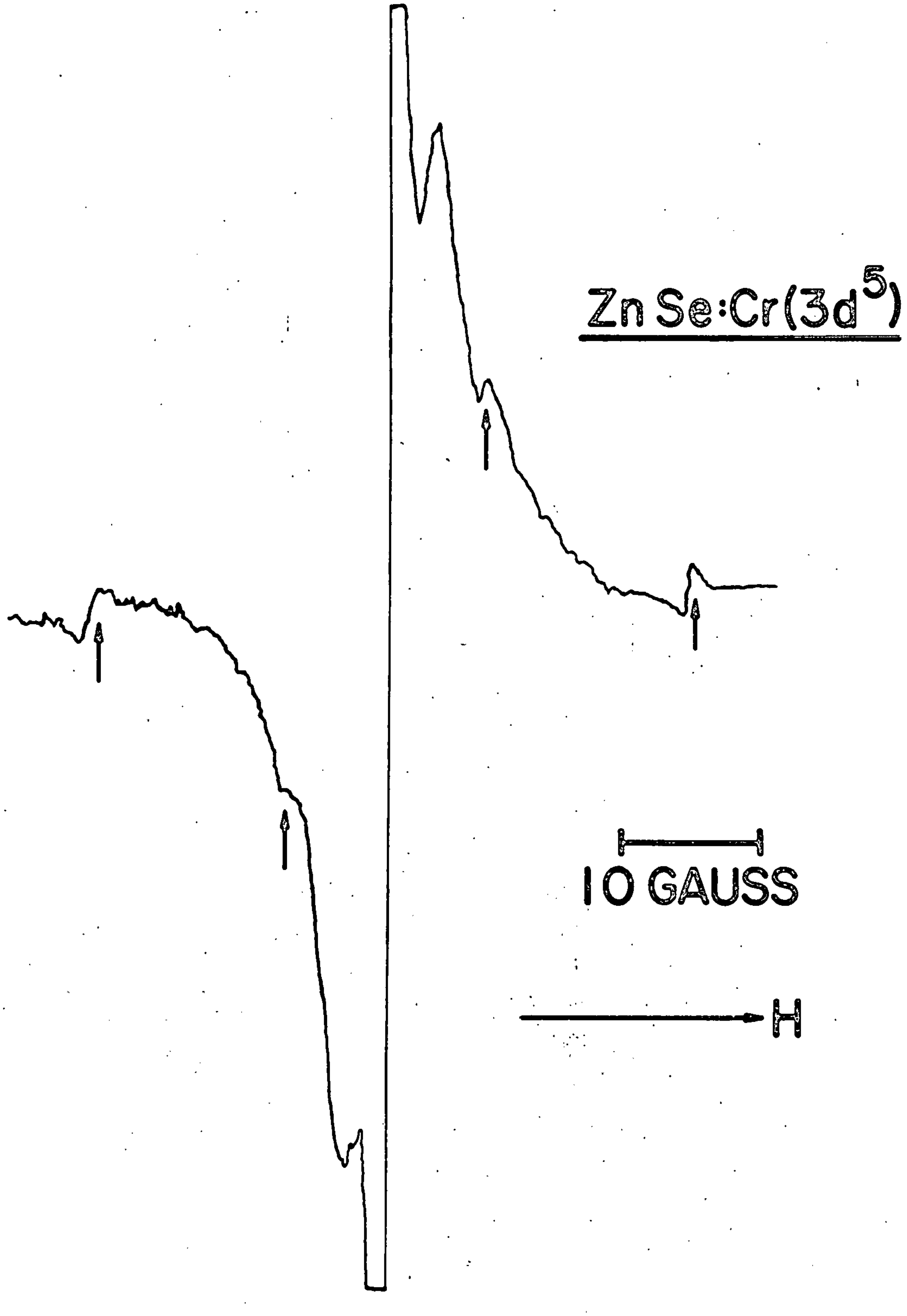

Figure 2 The paramagnetic resonance spectrum of ZnSe:Cr$^+$ taken with H in the (110) plane 30° from the [001] direction.

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