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Studies of a ^{2}E ground state V^{2+} ion in GaAs by TD-EPR

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Abstract. The problem of the ground state of a V^{2+} ion in GaAs is discussed once more. A V^{2+} centre, labelled as V^{2+}(II), with a $^4T_1$ ground state, has been observed previously by thermally detected electron paramagnetic resonance (TD-EPR) and identified as probably part of a complex. Further TD-EPR studies on GaAs:V are described here. They show a new line which is attributed to a V^{2+} centre having a ^{2}E ground state in agreement with the theoretical prediction for the isolated substitutional V^{2+} ion in this material. All the TD-EPR results and previous phonon scattering investigations on GaAs:V and GaP:V are compared. They appear to confirm this hypothesis.

1. Introduction

The problem of the ground states of the isolated V^{2+} ion in GaAs and GaP has been the subject of a number of theoretical and experimental investigations over recent years. 'Isolated' means that V^{2+} is at a gallium site without any other near-neighbour defect so that it does not belong to a complex. It has been predicted theoretically [1, 2] that the ground state is the low-spin ^{2}E instead of the high-spin $^4T_1$ expected from Hund's rule in the two materials.

The V^{2+} ion has been detected by optical absorption (OA) in both GaAs [3–5] and GaP [3, 6]. It gives rise to structureless bands from which it is difficult to deduce the exact nature of the ground state. The identification of the V^{2+} OA spectrum in GaAs has been confirmed by deep level optical spectroscopy (DLOS) measurements [7]. However, the isolated V^{2+} ion does not appear to have been observed previously by any technique based on electron paramagnetic resonance (EPR) in either GaAs or GaP.

We have studied the GaAs:V and GaP:V systems by thermally detected (TD) EPR (at X and Q bands) and we have obtained sets of lines identified as due to a V^{2+} centre having a $^4T_1$ ground state and assumed to be part of a complex [8–12] in both cases. This centre is labelled V^{2+}(II).

The aim of this paper is to present further TD-EPR results, obtained at 34.85 GHz, on a semi-insulating sample of GaAs:V. A new line, created by the illumination, is found which may be due to a V^{2+} centre having a ^{2}E ground state. However, before describing these results, we briefly recall some previous experiments related to V^{2+} centres in GaAs. Two of these favour a ^{2}E ground state for GaAs:V^{2+}. We also correlate the TD-EPR and phonon scattering data in GaAs:V and GaP:V.

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2. Previous studies on V^{2+} centres in GaAs and GaP

Until now, the strongest experimental proof for a ^2E ground state for V^{2+} in GaAs appears to be given by phonon scattering experiments. Comparison of the results obtained in GaAs [13] and GaP [14] containing 3d ions with T_1 and E ground states have shown that the scattering is strong in the cases of T_1-type ions but much smaller for E-type ions. The very weak scattering observed at frequencies greater than 100 GHz in GaAs:V is in marked contrast to the strong scattering seen in systems with states of T_1 symmetry and in GaP:V. From these results, it was deduced that the V^{2+} ground state is expected to be ^2E in GaAs [13] and $^4T_1$ in GaP [14].

A comparison of the weak photoionization scattering cross section σ_n^0 obtained in DLOS for the acceptor level of vanadium in GaAs with the theoretical values for 3d ions in InP [15] is also in favour of a ^2E ground state for V^{2+} in GaAs [7]. A V^{2+} centre has been observed in GaAs by optically detected magnetic resonance (ODMR) [16]. It gives an isotropic line with $g = 2.07$. However, its magnetic circular dichroism (MCD) spectrum [16] is different from that attributed to the isolated V^{2+} ion in OA and DLOS.

The results obtained from phonon scattering [13, 14] and TD-EPR [8–12] experiments on GaAs:V and GaP:V are summarized in table 1. The weak phonon scattering observed in GaAs:V and the intense peak seen in GaP:V, above 100 GHz, are indicated. However, in both materials, additional phonon scattering peaks are detected below 100 GHz. They give resonant frequencies which are close to the zero-field splittings (ZFSs) of the three lowest V^{2+}(II) levels. The latter were determined from the frequency dependences of the resonance lines in TD-EPR [8].

A trigonal model has been proposed for the V^{2+}(II) centre for both GaAs and GaP. It is assumed that the centre is a V^{2+} ion associated with a defect at a nearest-neighbour As or P site. Satisfactory agreement has been obtained in both cases for the fit of the experimental isofrequency curves at 34.85 GHz to those calculated using such a model for V^{2+}(II) and the ZFSs in the zero-strain approximation [11, 12]. Even if either the variations of the intensities of the V^{2+}(II) TD-EPR lines with the energy of the photon after illumination or the decay time of the illumination effect are those expected for the isolated V^{2+} ion in GaAs and GaP, such results can also be explained if V^{2+}(II) is associated and forms part of a complex [11, 12].

It is logical to attribute the low-frequency phonon scattering peaks and the sets of TD-EPR lines corresponding to the ZFSs of 4.0, 13.1 and 17.6 GHz in GaAs and 4.5, 12.2 and 16.7 GHz in GaP to V^{2+}(II). This conclusion is in agreement with the absence of a high-frequency phonon scattering peak in GaAs which suggests a ^2E state for isolated V^2 in this material.

It must be noted that another ZFS of 41.3 GHz has been determined from TD-EPR for GaP:V [12]. However, when it is used in the fit to the trigonal model, the agreement is not good, so the corresponding lines are not attributed to V^{2+}(II). A question then arises: can the peaks associated with the 41.3 GHz ZFS be due to the isolated V^{2+} ion? We return to this later.

3. New TD-EPR results in GaAs:V

Taking into account the results and interpretation presented above for GaAs:V, the isolated V^{2+} ion is expected to exhibit an EPR line with a behaviour similar to that of a $3d^1$ ion in GaAs or GaP (e.g. V^{4+} in GaP [17] or Ti^{3+} in GaAs [18] or GaP [19]). Therefore, in the

Table 1. Comparison between the phonon scattering and TD-EPR results observed in GaAs and GaP doped with vanadium.

	GaAs:V		GaP:V	
Technique	Below 100 GHz	Above 100 GHz	Below 100 GHz	Above 100 GHz
Phonon scattering	Peaks* → 6 and 20 GHz [13]	Weak phonon scattering; no peak [13]	Peak → 12 GHz [14]	Intense peak* → 380 GHz [14]
TD-EPR	Set of lines* → 4.0×, 13.1× and 17.6× GHz [8, 10, 11]	Line* $g = 1.96$ [this work]	Set of lines* → 4.5×, 12.2× and 16.7× GHz [8, 12]	Lines* → 41.3 GHz△ [12]
Possible identification	V^{2+}(II):$^4T_1$	Isolated V^{2+}:^2E	V^{2+}(II):$^4T_1$	Isolated V^{2+}:$^4T_1$

* The signals appear after illumination in the semi-insulating samples.
× The ZFS used for the fits to the trigonal model V^{2+}(II).
△ The fit to the trigonal model is not acceptable when this ZFS is used.

$g = 2$ region, we have looked for a TD-EPR line which could be due to the isolated V^{2+} ion. In this part of the spectra, different ions or other defects can give rise to several lines which overlap. For example, we have the V^{3+} and V^{2+}(II) signals, a line labelled as $\mathcal{J}$ due partially to the alumina (single-crystal) sample holder and also to the GaAs specimen, etc. The intensities of these lines depend upon the experimental conditions, the orientation of the sample in the magnetic field, the microwave power and also the illumination.

In particular, we have investigated the semi-insulating sample W1 of GaAs doped with vanadium (having a vanadium concentration of 3.4×10^{16} cm^{-3}) manufactured by Wacker Chemitronic which was studied in [11]. As usual in TD-EPR the resonance is detected via the heating of the sample, due to the spin–lattice relaxation, with a carbon thermometer at liquid ^{4}He temperatures. The experiments have been carried out at 34.85 GHz. The spectra obtained before illumination when the direction of the magnetic field $\boldsymbol{B}$ is close to the [001], [111] and [110] axes, are shown in figure 1. They exhibit the V^{3+} signal and the $\mathcal{J}$ line. Figure 2 shows that many lines appear after illumination (with a photon energy $h\nu_{exc} = 1.46$ eV). Most of the lines can be attributed to V^{2+}(II); for example, A_n and A when $\boldsymbol{B}$ is directed near to the [001] axis. In the $g = 2$ region, the situation is rather complicated after illumination. Close to the [001] axis, the spectrum is dominated by the A line (this very intense line is probably that observed in ODMR and reported in [16]). The weak signal seen at the V^{3+} line position is in agreement with the decrease expected for the V^{3+} resonance. When $\boldsymbol{B}$ is along the [111] axis, the latter is replaced by a rather intense signal, labelled as $\mathcal{V}$, which overlaps with $\mathcal{J}^*$. The * superscript on $\mathcal{J}^*$ indicates that a signal, from the GaAs sample, occurring at the same position as that of $\mathcal{J}$, is created or amplified by illumination. Again, $\mathcal{V}$ and $\mathcal{J}^*$ appear after illumination when $\boldsymbol{B}$ is parallel to the [110] axis. *However, with the experimental conditions corresponding to figure 2,* $\mathcal{J}^*$ dominates.

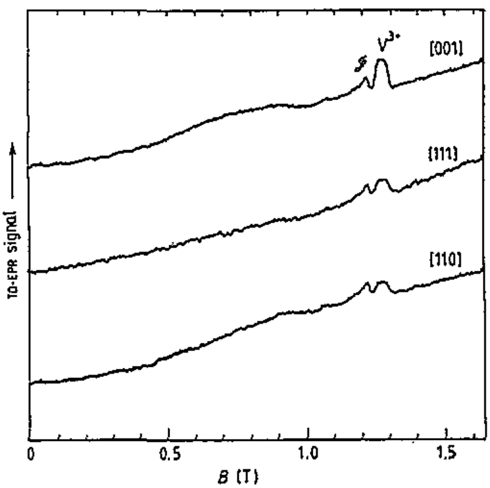

Figure 1. Thermally detected EPR spectra of GaAs:V (semi-insulating sample), at 34.85 GHz, for $\boldsymbol{B}$ close to the [001], [111] and [110] axes before illumination.

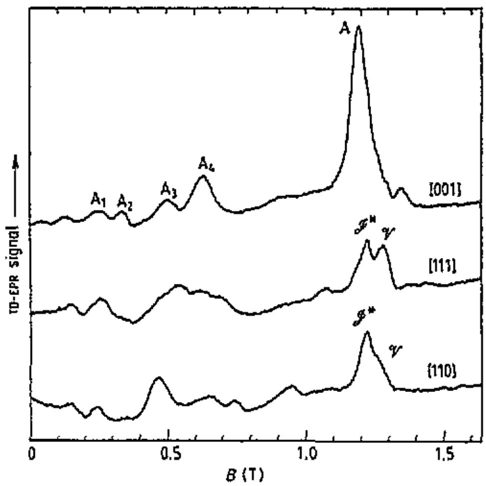

Figure 2. Thermally detected EPR spectra of GaAs:V (semi-insulating sample), at 34.85 GHz, for $\boldsymbol{B}$ close to the [001], [111] and [110] axes after illumination with light of energy $h\nu_{exc} = 1.46$ eV.

The spectral dependences (variations of the amplitudes versus the energy of the illumination photon $h\nu_{exc}$) of the A_4, A and V^{3+} signals have been studied in detail [11].

However, it is difficult to analyse accurately the different lines contributing to the spectra in the $g = 2$ region when $\boldsymbol{B}$ is along the [111] and [110] axes. This is because the spectrum consists of the sum of several overlapping resonances, some decreasing (e.g. V^{3+}) and others increasing (e.g. $\mathcal{V}$, $\mathcal{J}^*$) when $h\nu_{exc}$ increases. Nevertheless, we can deduce that, from the spectra obtained when $\boldsymbol{B}$ is parallel to the [110] axis, the $\mathcal{J}^*$ line is neither due to the isolated V^{2+} ion nor to the V^{2+}(II) centre, because, when $h\nu_{exc}$ is varied, its behaviour is different from that expected for these ions. It must be noted that a photoinduced signal such as $\mathcal{J}^*$ has been observed in most of the investigated samples of GaAs doped with vanadium which have been studied.

The spectra both before and after illumination have been obtained for different values of the microwave power P_{rf}. The amplitudes of the V^{2+}(II) and $\mathcal{J}$ signals increase more rapidly with P_{rf} than $\mathcal{V}$ (figure 3), indicating that the centre responsible for $\mathcal{V}$ is not so strongly coupled to the lattice as V^{2+}(II) (which has a $^4T_1$ ground state). Furthermore, from comparison of the behaviours of the $\mathcal{V}$ and V^{3+} signals (after and before illumination respectively) when $h\nu_{exc}$ is varied, it appears that V^{3+} (having an A_2 ground state) is more weakly coupled than is the centre giving rise to $\mathcal{V}$. From these results, it can be expected that either the $\mathcal{V}$ line comes from a centre having an E ground state or that a cross relaxation effect, involving V^{3+} and such a centre, leads to a decrease of the V^{3+} relaxation time then to an increase of the V^{3+} signal [20]. However, the first hypothesis appears more reasonable because we have not been able, so far, to observe any clear cross relaxation effect in TD-EPR spectra from III–V crystals.

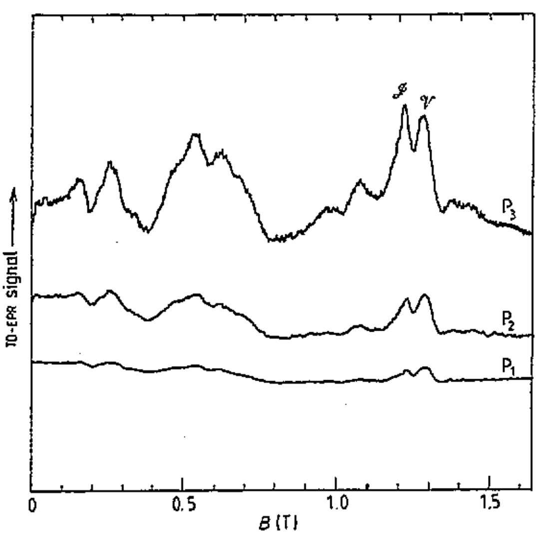

Figure 3. Evolution with the microwave power, P_{rf}, of the thermally detected EPR spectrum of GaAs:V, after illumination ($h\nu_{exc} = 1.46$ eV), for $\boldsymbol{B}$ near to the [111] axis, at 34.85 GHz. The increase of the intensities of the V^{2+}(II) lines (unlabelled) and of $\mathcal{J}$ with P_{rf} is more rapid than that of line $\mathcal{V}$ ($P_{rf} = P_n$, $n = 1, 2, 3$; $P_1 < P_2 < P_3$).

Figure 4 shows the spectra obtained after illumination for different values of the angle θ between $\boldsymbol{B}$ and the [001] axis, with $\boldsymbol{B}$ rotated in the $(1\bar{1}0)$ plane, using a small microwave power in the range available. In the conditions of the experiment, $\mathcal{J}^*$ is not seen or it is very weak depending upon the orientation of the sample. It must be noted that the intensity of $\mathcal{J}^*$ varies with the 'history' of the sample (cooling, illumination etc). The V^{2+}(II) resonances are small because of the low microwave level. The spectra shown in figure 4 exhibit the $\mathcal{V}$ line; the latter is nearly isotropic in position and dominates the V^{3+} signal which is very weak (so that it cannot be due to V^{3+} only).

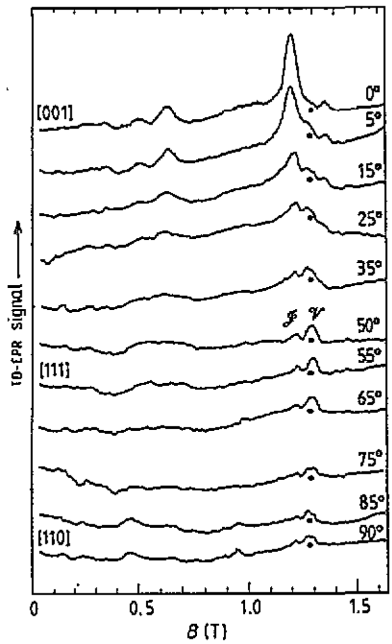

Figure 4. Thermally detected EPR spectra of GaAs:V (semi-insulating sample), at 34.85 GHz, after illumination ($h\nu_{exc} = 1.33$ eV), for different orientations, with ***B*** rotated in the ($1\bar{1}0$) plane. The values of angles indicated are those between ***B*** and the [001] axis.

Another test of the nature of the ground state of the $\mathcal{V}$ line is to measure the angular variation of its linewidth. This is rather difficult in this particular case and an alternative is to measure the zero-to-peak intensity I_{0p} of the TD-EPR resonance line. I_{0p} characterizes the line shape of the EPR line which is related to the simultaneous action of the random strain effects within a $E \otimes e$ Jahn–Teller (JT) effect [21]. The angular dependence of the linewidth and consequently also of I_{0p} is determined primarily by random strain effects [19]. Thus the zero-to-peak intensity I_{0p} of $\mathcal{V}$ has been extracted (after some deconvolutions) from the spectra and recorded every 5°; the result is shown in figure 5. It can be seen that I_{0p} passes through a maximum when the direction of ***B*** is close to the [111] axis. Also, the main minimum in I_{0p} is observed when ***B*** is along the [001] axis and a second subsidiary minimum occurs when ***B*** is parallel to [110]. This anisotropy is in excellent agreement with that expected for EPR in a ^2E state [19, 21] and thus we conclude that $\mathcal{V}$ has a ^2E ground state.

A more conducting n-type sample of GaAs doped with vanadium, containing isolated V^{2+}, has also been studied at 34.85 GHz with a small value of P_{rf}. Its TD-EPR spectra also show the $\mathcal{V}$ line very clearly when θ is in the 40–70° range, within a maximum in the intensity when ***B*** is along the [111] axis.

4. Discussion and conclusion

Three important points have been observed for the new $\mathcal{V}$ line in GaAs:

(i) The spin–lattice coupling of the centre responsible, which is weaker than that of the $^4T_1$ V^{2+}(II) centre not larger than that of $^3A_2$ V^{3+}, suggests an E state.

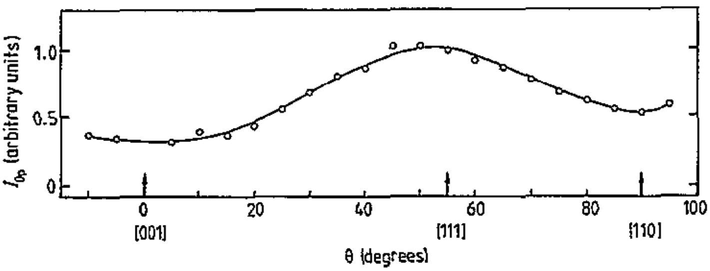

Figure 5. The angular variation of the zero-to-peak intensity I_{0p} for the $\mathcal{V}$ line when $\boldsymbol{B}$ is rotated in the $(1\bar{1}0)$ plane.

(ii) The angular variation of I_{0p} reflects that found with a ^{2}E ground state such as that observed for V^{4+} and Ti^{3+} in GaP (conventional EPR [17, 19]) and Ti^{3+} in GaAs (TD-EPR below 4 K).

(iii) It seems to be strongly V^{2+}-related, either appearing after illumination in a semi-insulating sample, or being present together with the isolated V^{2+} ion in a semiconducting specimen.

Thus from these results, it is possible to attribute the $\mathcal{V}$ signal to a ^{2}E ground state V^{2+} ion with a g value of 1.96.

The TD-EPR data clearly support the phonon scattering results that the ground state for the isolated V^{2+} ion is probably ^{2}E in GaAs and $^4T_1$ in GaP. With such a conclusion, the corresponding TD-EPR lines could be the $\mathcal{V}$ line for GaAs and the set of resonances involving the ZFS at 41.3 GHz for GaP as indicated in table 1. $\mathcal{V}$ exhibits an angular dependence characteristic of an $E \otimes e$ JT effect in the presence of random strain [21]. In GaP, an orthorhombic JT $T_1 \otimes (e + t_2)$ effect was suggested from the phonon scattering results [14]. Such a model might indeed explain our experimental data but it is difficult to give a definitive proof of it. At this stage, the only possible problem with these attributions is that the optical absorption band spectra in the 1.0 to 1.1 eV region from isolated V^{2+} in GaAs and GaP look very similar to each other even though we are supposing that the ground states are different. However, the observed OA band is structureless (confirmed by our own TD-OA experiments for GaAs [22] and for GaP [12, 22]). This does not therefore conflict with our assignments as line shapes of broad bands are generally very insensitive to the detailed structure of the ground state wavefunctions and depend much more on the effects of vibronic coupling associated with the ground states and with all the excited states involved to which transitions occur. Furthermore, in reality, the V^{2+} ground state will involve admixtures via spin–orbit coupling of both ^{2}E and $^4T_1$ states; the probable situation is that, in the case of GaAs, the contribution from ^{2}E just dominates but, for GaP, $^4T_1$ dominates. Whereas phonon scattering and TD-EPR experiments are very sensitive to the details of the ground states, OA is not.

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