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Vanadium in CdTe: An electron-paramagnetic-resonance study

P. Christmann and B. K. Meyer
Technische Universität München, Physik Department, E16, 85747 Garching, Germany

J. Kreissl
Technische Universität Berlin, AG EPR am Institut für Festkörperphysik, 12484 Berlin, Germany

R. Schwarz and K. W. Benz
Albert Ludwigs Universität Freiburg, Kristallographisches Institut, 79104 Freiburg, Germany

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The transition-metal ion vanadium in CdTe is studied using electron paramagnetic resonance (EPR) and photo-EPR. Based on the observation of central hyperfine interaction, the EPR measurements identify two vanadium related defects. They are assigned to V^{3+} and V^{2+}, both substitutional for Cd. Whereas V^{3+} shows the classic isotropic EPR spectrum, the V^{2+} spectrum features triclinic symmetry caused by a strong Jahn-Teller coupling to both τ_2 and ϵ vibronic modes. By means of photo-EPR the V^{2+}/V^{3+}-donor level is determined at 0.67 eV below the conduction band.

I. INTRODUCTION

In the last years, CdTe doped with vanadium has received wide interest, due to the discovery of photorefractive behavior of this material.[1–3] For photorefractive applications CdTe is especially well suited, as it possesses a very high electro-optical coefficient.[1] Doped with transition-metal elements (e.g., Ti, V) it shows strong absorption bands in the near-infrared spectral range.[4] For photorefractive behavior it is necessary that the centers responsible for the absorption are rechargeable. This means that they introduce an energy level in the band gap and exist at least in two different charge states. For vanadium the two charge states V^{3+} and V^{2+} are expected; i.e., vanadium should act as a donor in CdTe. Indeed, vanadium is considered responsible for the high resistivity of CdTe crystals.[5] Using photoconductivity a level at $E_{CB}-0.78$ eV was found, identified with the V^{2+}/V^{3+}-donor level.[6] However, for vanadium incorporated on substitutional cation sites, so far only the singly positive charge state V_{Cd}^{3+} $(A^+,3d^2)$ was detected with the help of electron paramagnetic resonance (EPR).[7–10] This is an unpleasant situation and one can of course argue that: (i) The V^{2+}-EPR signal is broadened beyond detection by internal strain.[7] (ii) V^{2+} has an extremely short spin-lattice relaxation time, possibly due to a Jahn-Teller effect acting on the low-spin $3d^3$ ground state. (iii) The V^{2+}/V^{3+} level could be resonant with the conduction band—less likely, since this is incompatible with the high resistivity of CdTe:V and the photoconductivity experiments.

It was therefore our aim, using EPR and photo-EPR, to determine whether or not the V^{2+} charge state exists, to determine, if possible, its magnetic resonance properties, and to conclude about the level position.

II. EXPERIMENTAL DETAILS

The investigated CdTe:V crystals were grown by the vertical Bridgman technique at a growth temperature of about 1130 °C. The dopant V was added to the synthesis in a concentration of 5×10^{18} cm^{-3}. The incorporation of the transition metal into the CdTe lattice was nearly one order of magnitude lower. Due to the small segregation coefficient (2×10^{-3}) the V concentration increased in the growth direction from the beginning to the end of the crystal from 4×10^{17} up to 8×10^{17} cm^{-3} as determined by secondary-ion-mass spectroscopy measurements. Parallel to the concentration profile the resistivity distribution increased from 7×10^{8} up to 1×10^{10} Ω cm. For our EPR studies we used samples cut from the region with the highest V concentration.

The EPR and photo-EPR measurements were performed at X-band frequencies (9.5 GHz) using a Bruker ESP 300 E spectrometer equipped with a helium-gas flow cryostat. Light illumination of the sample for the photo-EPR measurements was achieved by combining a halogen lamp and a high-throughput monochromator.

III. EXPERIMENTAL RESULTS AND DISCUSSION

In Fig. 1 the EPR spectrum of a vanadium-doped sample is shown for the applied magnetic field parallel to a $\langle 110\rangle$ crystal axis and simultaneous illumination with light of energy 1.15 eV. The octet of very intense resonance lines has been assigned to V^{3+} $(A^+,3d^2)$.[7–10] The splitting into eight lines is caused by hyperfine interaction with the vanadium nucleus ^{51}V $(I=7/2$ with 99.75% abudancy). The smaller lines can be bundled into three groups of eight lines each, again featuring the characteristic V hyperfine structure. The hyperfine splitting is $A_V=60\times10^{-4}$ cm^{-1}, i.e., within experimental accuracy identical to the one of V^{3+}.

It turns out that the eightfold split line groups are anisotropic. Their angular dependence for a rotation in a $\{110\}$ crystal plane is shown in Fig. 2. The center of gravity of each octet is represented by a square. The experimental angular dependence can be explained only by assuming a triclinic symmetry. In triclinic symmetry 12 magnetically different

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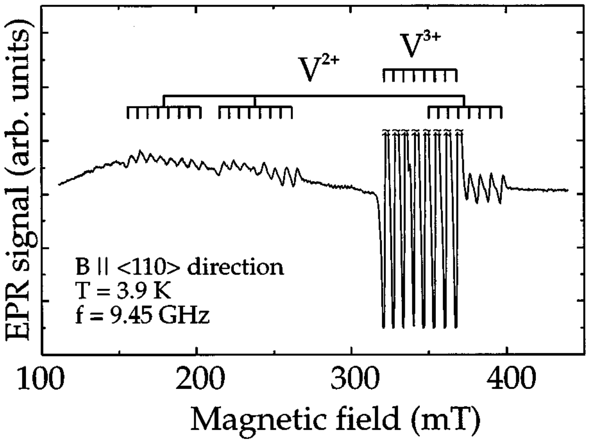

FIG. 1. Under illumination with light of 1.15 eV the EPR spectra of V^{2+} and V^{3+} are simultaneously observable. The V^{2+} resonance lines can be bundled into three groups. Four lines of the high-field group are superimposed by the more intense V^{3+} lines and thus not resolved. The hyperfine splitting is identical for both charge states.

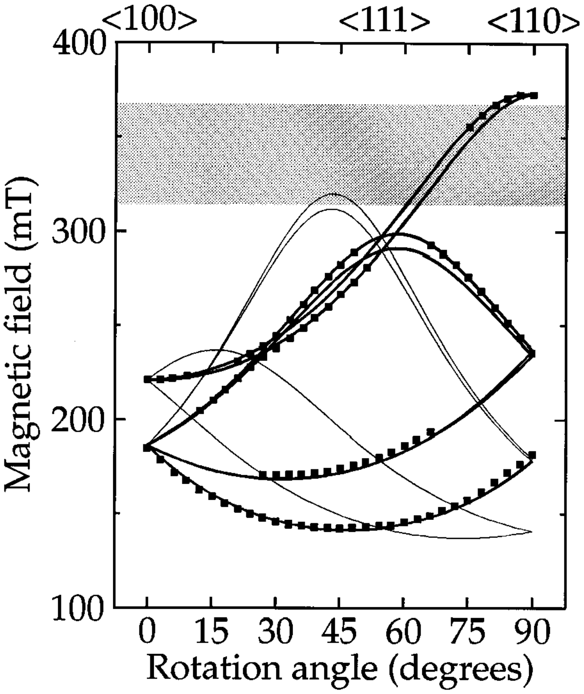

FIG. 2. Squares: Angular variation of the centers of gravity of the eightfold split line groups for a rotation in a {110} plane. Solid lines: Simulation of the V^{2+} angular dependence. For the simulation a triclinic symmetry was assumed. The parameters of the spin Hamiltonian are given in the text. The thickness of the simulated lines is proportional to the calculated transition probability. Only those octets which correspond to a high transition probability are observed. Between 320 and 370 mT the more intense V^{3+} lines cover the V^{2+} lines.

center positions are expected for a rotation in a {110} crystal plane.

The spectrum with triclinic symmetry is assigned to V_{Cd}^{2+} $(A^0,3d^3)$, i.e., the neutral donor-charge state of vanadium, on the basis of the following arguments. The V^{2+} ground state is a $^4T_1$ state in a tetrahedral crystal field and is hence expected to undergo a Jahn-Teller effect.

V^{2+} in ZnS and Cr^{3+} in GaAs are typical examples where Jahn-Teller distortions result in low symmetry and anisotropic EPR spectra. In the case of V^{2+} in ZnS, the observed trigonal symmetry was explained by a $T\otimes\tau_2$ Jahn-Teller coupling.[11] For Cr^{3+} in GaAs, an isoelectronic system, an orthorhombic distortion was reported, resulting from a Jahn-Teller coupling to both τ_2 and ϵ vibronic modes, as can be expected for V^{2+}.[12] The lowering from orthorhombic (coupling to τ_2 and ϵ) to triclinic symmetry is explained by an additional off-center movement of the V^{2+} ion. It should be noted here that the general features of the spectrum, i.e., hyperfine splitting, symmetry, and its interpretation, are identical to the case of V^{2+} in ZnTe.[13]

The Jahn-Teller distortion results in a splitting of the $^4T_1$ state into three orbital singlets $^4B_1$, $^4B_2$, and $^4A_2$. The $^4A_2$ is the energetically lowest and has a fourfold spin degeneracy $(S=3/2)$. It is further split by spin-orbit interaction in $|\pm 1/2\rangle$ and $|\pm 3/2\rangle$ spin substates. The appropriate spin Hamiltonian for an interpretation of the angular dependence of the V^{2+} EPR consists therefore of Zeeman and fine-structure terms (the hyperfine interaction is omitted):

$$H=\mu_B\vec{B}\tilde{g}\vec{S}+\vec{S}\tilde{D}\vec{S}, \tag{1}$$

with the g tensor $\tilde{g}$ and the fine-structure tensor $\tilde{D}$. All other symbols have their usual meaning. In its principal axis system ($z'\|[-0.703\ 0.710\ -0.027]$, $y'\|[0.678\ 0.681\ 0.277]$, $x'\|[-0.215\ 0.1760\ 0.960]$) $\tilde{g}$ consists of the diagonal elements $g_{z'}=2.0023$, $g_{y'}=1.98$, and $g_{x'}=1.99$. Note that the deviation of the quantization axis z' from the monoclinic $\langle 110\rangle$ direction is small, as can be seen in the small value -0.027. The fine-structure tensor $\tilde{D}$ consists of the parameters D and E.[14] In our analysis D turns out to be larger than 1 cm^{-1}. Therefore we can only put a lower limit for D, i.e., $D>1$ cm^{-1}. In this case only the ratio of E/D has an influence on the simulation. The ratio is determined to be $E/D=0.188$ cm^{-1}. The angular dependence of the resonance line positions obtained using this spin Hamiltonian is plotted together with the experimental data in Fig. 2. The calculated transition probabilities are indicated by the corresponding line thicknesses. Only those resonance lines are experimentally observed that correspond to a high transition probability. The agreement between calculation and experiment for the angular variation is quite satisfactory, especially if one takes into account the large number of resonance lines. Hence in the following we assume that we have observed the V^{2+} EPR, but by additional photo-EPR experiments we strengthen the evidence.

Without illumination of the sample only the V^{3+} charge state of vanadium was observable. By illumination with white light the V^{2+}-EPR signals are emerging, while the V^{3+} signal is decreasing. This observation implies that the Fermi level that governs the occupation of the charge states is located below the V^{2+}/V^{3+} energy level (see Fig. 3). The decrease in the V^{2+}-EPR signals can be caused by two processes:

$$V^{3+}+h\nu\rightarrow V^{2+}+h_{VB}^{+}, \tag{2}$$

or

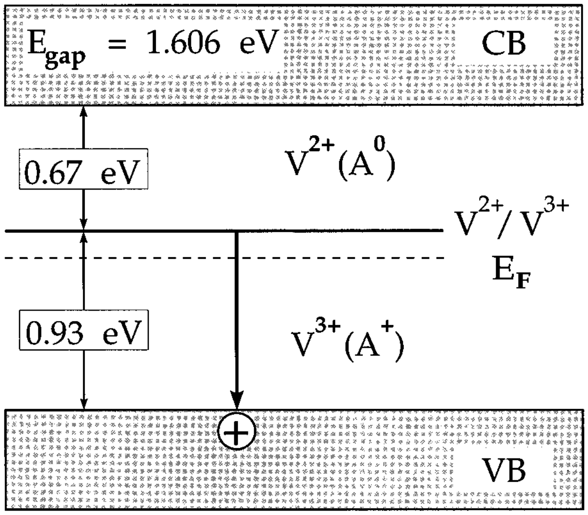

FIG. 3. Energy-level scheme of the V^{2+}/V^{3+} level in the band gap of CdTe. The Fermi level is assumed to be below this level. The vanadium recharging process is a hole emission to the valence band: $V^{3+}+h\nu\rightarrow V^{2+}+h^{+}_{\mathrm{VB}}$.

$$X^{-}\rightarrow X^{0}+e^{-}_{\mathrm{CB}},$$

$$e^{-}_{\mathrm{CB}}+V^{3+}+h\nu\rightarrow V^{2+}. \tag{3}$$

X denotes a defect (so far unspecified) that exchanges electrons with V^{3+}. It should be of acceptor type, either of extrinsic or intrinsic origin. Whereas intrinsic acceptors such as the Cd vacancy are commonly not observed in as-grown CdTe, the residual shallow acceptors P, As, Ag, and Cu are common impurities in CdTe. They might be present in a total amount of $N\leqslant 10^{17}$ cm^{-3}, explaining why undoped CdTe usually shows p-type conduction. This is in line with the observation of V^{3+} in the dark. The acceptor binding energies range between approximately 60 for P and 150 meV for Cu, and one can expect the recharging process $A^{-}+V^{3+}+h\nu\rightarrow A^{0}+V^{2+}$ to start close to the energy gap of CdTe ($E_g=1.606$ eV, $T=4.2$ K).

The signal intensity of V^{2+} as a function of photon energy (steady-state technique), where the photon flux was held constant during the measurements is shown in Fig. 4 on a logarithmic scale. As can be seen, the V^{2+}-EPR signal is rising at light energies of approximately 0.95 eV. A fit to the experimental data within the Ridley model[15] is shown as a solid line. It does correctly reproduce the increase of the cross section near the threshold energy and the resulting optical trap depth is obtained as $E_T=0.93\pm 0.005$ eV. It does not correctly reproduce the slight decrease of the cross section at higher energies. Since we are dealing with an optical experiment, i.e., determining the optical cross section and not monitoring the thermal release of the carriers as in a deep-level transient experiment, lattice relaxation effects are not included. They could be in the order of 0.1–0.2 eV. Apart from these steady-state studies the time transients of the V^{2+} signal rise were analyzed by the initial-slope technique.[16] Both evaluations gave within experimental accuracy the same result.

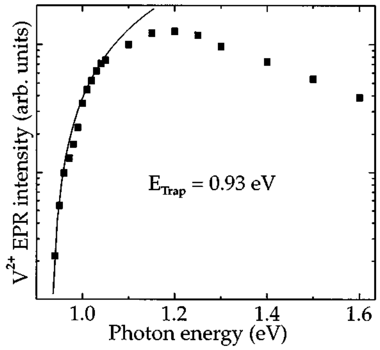

FIG. 4. Energy dependence of the photogeneration of the V^{2+}-EPR signal. The experimental data are shown as squares and a fit according to the Ridley model is shown as drawn line. The resulting optical trap depth is $E_T=0.93\pm 0.005$ eV.

The trap depth rules out that shallow acceptors are involved, also the Cd vacancy cannot act as a source for electrons. Its binding energy is less than 400 meV above the valence band. All this lets us conclude that the recharging occurs between the two charge states of vanadium. A more decisive argument would, of course, be to monitor the concentration of V^{3+}, its decrease by light illumination, and the corresponding increase of $N_{V^{2+}}$. However, due to distinct differences in spin-lattice relaxation times for both charge states this experiment was not possible. The $^{3}A_2$ ground state of V^{3+} ($S=1$) has a long spin-lattice relaxation time. For a microwave power of 0.2 μW a reduction of 50% of the V^{3+} EPR signal could be seen under light illumination. However, at low microwave powers, the V^{2+} signal is no longer observable. Since the V^{3+} concentration (in the dark) was of the order of 5×10^{17} cm^{-3} and changes of the order of 50% have been induced by light illumination, extrinsic impurities acting in the recharging process can safely be ruled out. This is of importance since *a priori* we cannot decide whether the origin of the lowering from T_d symmetry to triclinic is caused by a static Jahn-Teller effect or by an associated defect. But the assignment of the spectrum to isolated V^{2+} is furthermore supported by the following arguments: First, transition-metal pair defects, well documented in II-VI compounds,[17,18] predominantly involve the positively charged donor, i.e., V^{3+}. The associated defect is bound by Coulomb interaction (extrinsic acceptor in the singly negative charge state). The pairs are hence neutral and electrically inactive. Second, the EPR of V^{2+} does not saturate at intermediate powers (≈ 2 mW) at 4 K. This behavior of a strong coupling to the lattice is typical for Jahn-Teller ions. Third, the signal intensity is decreasing for temperatures above 12 K by line broadening. Fourth, strong evidence comes from the recharging experiments, described above. And finally, against a pair defect speaks that for both V centers the same hyperfine splitting is observed.

IV. CONCLUSIONS

In conclusion, we have presented strong evidence that vanadium exists in two different charge states, V^{3+} (A^{+},$3d^{2}$)

and V^{2+} (A^0,$3d^3$); i.e., it forms a donor-type defect. For both charge states central hyperfine interaction with the $I=7/2$ ^{51}V nucleus was observed. The splitting is within experimental accuracy identical. From photo-EPR experiments we have no indications that extrinsic or intrinsic impurities are involved in the recharging of the V^{3+} and in the built up of the V^{2+} EPR signal. Based on concentration arguments and the number of extrinsic-extrinsic acceptors present in CdTe, we are led to conclude that V^{2+} shows triclinic symmetry, and that the V^{2+}/V^{3+}-donor level is located at $E_{CB}-0.67$ eV.

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