Origin of the 6885-cm^{-1} luminescence lines in ZnO: Vanadium versus copper

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Optical detection of electron paramagnetic resonance reveals the $I=7/2$ EPR spectrum of V^{2+} in the sharp photoluminescence (PL) lines often observed at ~6885 cm^{-1} in ZnO, which have universally been assumed previously to arise from copper. An alternative model for the origin of the lines is tentatively presented therefore which involves vanadium as a trace impurity rather than copper. An additional $I=7/2$ spectrum, of unknown origin, is also detected both in these lines and in the stronger visible PL of the material.

INTRODUCTION

A sharp set of photoluminescence (PL) lines in ZnO with prominent zero phonon line (ZPL) at ~6885 cm^{-1} has been studied by several groups.[1–4] It has universally been assumed by these authors that they arise from the impurity copper, although conflicting models have had to be presented to try to account for the details of the electronic transitions involved. In particular, one of the difficulties in any simple model has been the fact that the 6885 cm^{-1} ZPL is higher in energy than the known 5821, 5784 cm^{-1} absorption doublet for substitutional Cu^{2+},[5] which should excite the expected transitions if it is associated with isolated substitutional Cu^{2+}, the logical choice. (Throughout this paper we will use the ionic convention for denoting the charge state, Cu^{2+} substituting for Zn^{2+}, as has been the convention in most optical and EPR publications concerning ZnO. In its semiconductor role, it is, of course, [Cu]^0.) Considering the various suggested models, Schulz and Thiede[4] concluded that the best solution is that of an internal transition within a different charge state Cu^{3+}, which allowed them to account for the transitions with their polarization properties. Such a model had been suggested earlier,[2] but then rejected using the argument that a stable charge state of Cu^{3+} was unlikely, and a donor-Cu^{2+} pair was suggested instead.[3] In all cases, it has been assumed to be associated with copper, even though it apparently is often seen in samples not intentionally doped with copper.[4]

Here we report a study using optical detection of electron paramagnetic resonance (ODEPR) in the photoluminescence (PL) of a single crystal of ZnO, which displays the 6885 cm^{-1} PL lines. In it, we find that the dominant ODEPR signal detected in the PL system is unambiguously identified with V^{2+}. No ODEPR spectrum associated with copper is observed. This suggests that the luminescence may actually be associated with vanadium, not copper.

I. EXPERIMENTAL PROCEDURE

The sample studied was cut from a single c-axis hexagonal crystallite grown from the vapor phase at the Institute for Applied Physics, University of Erlangen, Germany.[6] It was not intentionally doped. Most of the PL and PLODEPR studies were performed under excitation with the ultraviolet (UV) lines (351.1, 363.8 nm) available from an Ar$^+$ ion laser. The typical excitation power was ~20 mW. Detection of the luminescence was achieved in the visible and near-UV by a silicon diode (EGG 250 UV) and in the near-IR by a cooled Ge detector (North Coast EO817S), followed by lock-in detection synchronized to the frequency of a chopper in the excitation (for PL), or to the microwave on-off modulation frequency (for PLODEPR). All PL and PLODEPR studies were performed on pumped liquid He (~1.7 K) in a 35 GHz ODEPR spectrometer which has been described elsewhere.[7] The spectral dependence of the PL was determined by placing a 1/4 m Jarrell-Ash monochromator before the detector, with subsequent correction for the spectral response of the monochromator and detector. The spectral dependence of the ODEPR signals was determined by placing selected absorptive and/or interference filters before the detector.

II. EXPERIMENTAL RESULTS

The PL observed in the sample under UV excitation is shown in Fig. 1. In the visible region, the PL is dominated by a strong broad slightly structured green band centered at ~530 nm, which appears similar to that established for many years as arising from a bound exciton state of Cu^{2+}.[9] Seen, much weaker in the near UV, are the neutral donor bound exciton (DBE) and distant donor-acceptor (DA) bands. In addition, as shown in the figure, a set of sharp lines in the near IR are observed, which are identical, within our resolution accuracy, to the much studied 6885 cm^{-1} bands. Differences in the relative amplitudes of the individual lines compared to previously published results are readily accounted for by the lower resolution in the present studies, which, for example, greatly enhances the broader phonon replicas of the 6885 cm^{-1} ZPL line. The relative spectral positions of the lines also agree, the measured separation in Fig. 1 between the 6885 cm^{-1} line and the sharp lowest energy line at 6280 cm^{-1} is 605 cm^{-1}, which is to be compared, for example, with 594 cm^{-1} reported by West *et al.*,[3] and 617 cm^{-1}
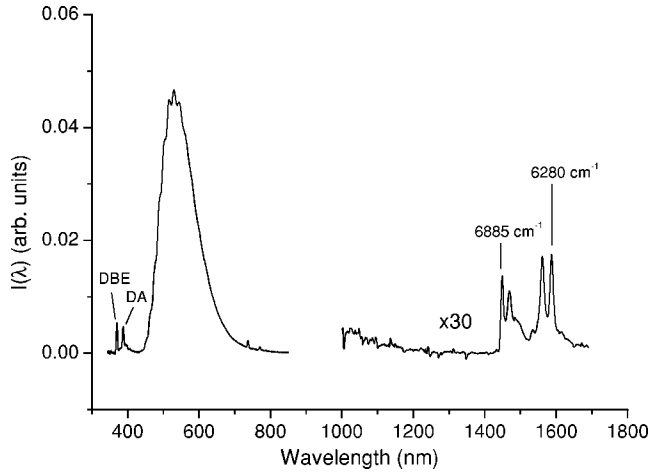
FIG. 1. PL spectrum at 1.7 K under excitation at 351.1 nm.

by Schulz and Thiede.[4] (The differences between the spectral positions reported by the different groups are greater than the reported accuracy by each and has been a subject of concern as to the origin of the differences.[4] However, it is clear that the set of bands in our sample is the same as has been studied by the various workers, and assumed to be of the same origin and copper related.) The 6885 cm^{-1} lines are also effectively excited by all of the visible Argon ion laser lines (459.7 to 514.5 nm), but the strong 530 nm band requires UV excitation.

In Fig. 2, we show the ODEPR spectrum observed under UV excitation with a filter that passes only all wavelengths detected by the Ge detector longer than 1250 nm. Most of
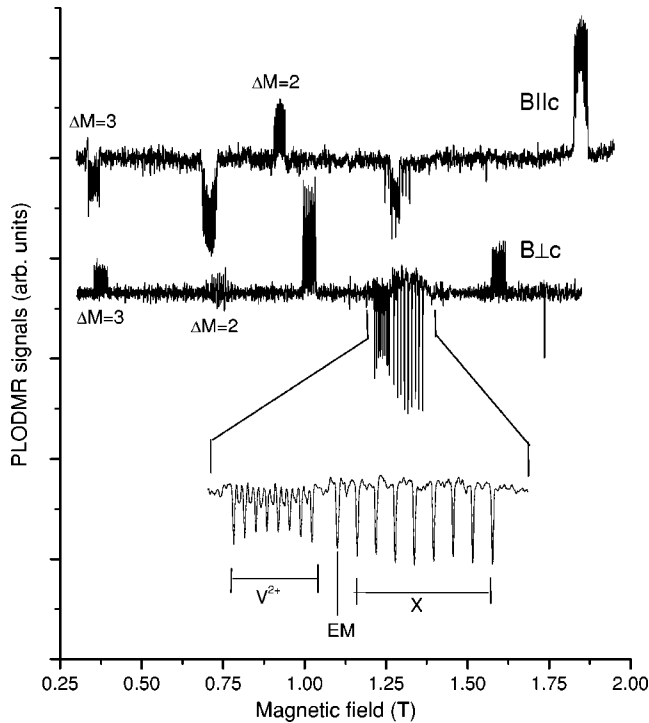

FIG. 2. ODEPR spectrum observed at $T=1.7$ K for wavelengths beyond 1250 nm under 363.8 nm excitation. The microwave frequency was 34.844 GHz.
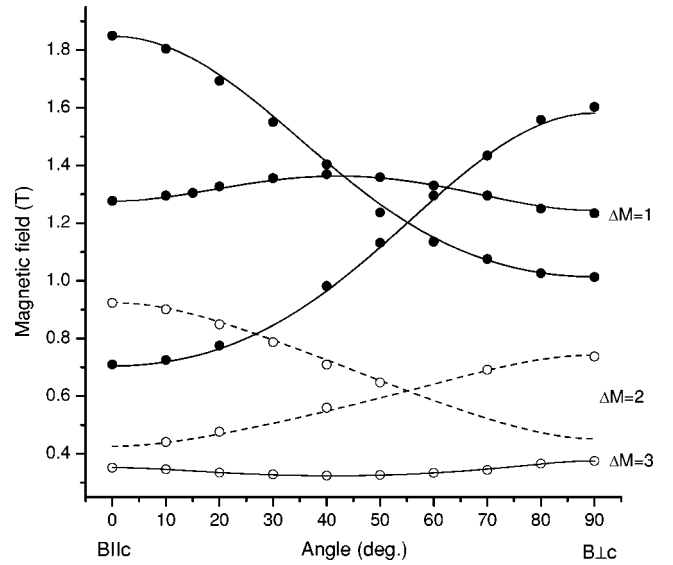

FIG. 3. Angular dependence of the V^{2+} ODEPR spectrum. The points are the measured positions for the center of the hyperfine multiplets. The lines give the angular dependence predicted using previously established values of g and D for V^{2+} (Ref. 10), as given in Table I.

the lines arise from the allowed ($\Delta M = \pm 1$) and forbidden ($\Delta M = \pm 2, \pm 3$) transitions of a single electronic spin $S = 3/2$ spectrum which display the additional splittings of hyperfine interaction with a ~100% abundant nucleus of spin $I = 7/2$. The spectrum can be described by the axially symmetric spin Hamiltonian

$$\mathcal{H} = \mu_B g_\parallel B_z S_z + \mu_B g_\perp (B_x S_x + B_y S_y) + D(S_z^2 - S(S+1)/3)$$
$$+ A_\parallel S_z I_z + A_\perp (S_x I_x + S_y I_y), \tag{1}$$

where μ_B is the Bohr magneton, **B** is the magnetic field, and "$\parallel$" and "z" refer to the crystal c axis. [Shown on an expanded magnetic field scale, for **B** $\perp c$ axis, is the simple eight line hyperfine structure ($2I+1$) for one of the transitions. At arbitrary orientation of **B**, the structure becomes much more complex with the emergence of strong "forbidden" nuclear spin flip transitions resulting from the large fine-structure D term which causes the hyperfine field seen by the nucleus to depart significantly from the electron spin quantization axis.] Figure 3 shows the angular dependence of the magnetic field for the center of the hyperfine structure measured for each transition, and compares it to the values predicted from the D and g values for V^{2+} in ZnO given in Table I, which were established from earlier EPR studies.[10] This, plus the close agreement of the measured hyperfine parameters with the EPR values also included in Table I confirms unambiguously that the spectrum arises from V^{2+}.

Another spectrum observed in Fig. 2, which we tentatively label X, also reveals $I=7/2$ hyperfine structure, as also shown in the expanded scale inset. It is simpler and, analyzed as an $S=1/2$ spectrum, gives the values also presented in the table. It does not appear to have been reported before. It is also probably vanadium-related, perhaps in some type of complex, or as a photogenerated excited $S=1/2$ state of iso-

TABLE I. Spin Hamiltonian parameters. The units for D and A are 10^{-4} cm^{-1}.

Spectrum	S	I	g	$|D|$	$|A|$
$(V^{2+})^a$	3/2	7/2	$g_\parallel=1.951(1)$	2606.8(1.0)	$A_\parallel=42.9(0.5)$
			$g_\perp=1.923(1)$		$A_\perp=46.4(0.5)$
X	1/2	7/2	$g_\parallel=1.939(1)$		$A_\parallel=93.6(1.0)$
			$g_\perp=1.881(1)$		$A_\perp=91.5(1.0)$

^{a}Reference 10.

lated V^{2+}, but we cannot, of course, rule out a different trace $\sim100\%$ abundant $I=7/2$ element, of which there are several. Also observed, as shown in Fig. 2, is the shallow donor effective mass (EM) resonance.[8]

Spectral dependence studies for the V^{2+} ODEPR spectrum reveal its detection only in the 6885 cm^{-1} set of lines. It is absent in the much stronger visible and near-UV luminescence. In addition, by selective filters, it was demonstrated to be equally divided between the two halves above and below ~1520 nm (6579 cm^{-1}), assuring that V^{2+} is being observed in, and only in, the complete set of lines. The other spectrum X is observed also weakly in the visible spectrum as well. Both spectra are present only under UV excitation. (With the exception of weak X and EM signals, no additional prominent ODEPR lines are observed in the strong visible PL.)

III. DISCUSSION

Copper is probably present in the crystal, as evidenced by the dominance of what appears to be its characteristically structured green luminescence band. However, a careful search in both the visible and near-IR has revealed no ODEPR spectrum that could be related to Cu^{2+}, for which the EPR spectrum of its ground state is well established.[5] This, by itself, proves only that spin-dependent capture of a carrier (electron or hole) by Cu^{2+} in its ground state is not a rate limiting process in the pumping cycle for either of the PL bands. In particular, the copper green luminescence has been identified as a transition from an excited state, composed of $Cu^{1+}(d^{10})+$a deep bound hole, to the ground $Cu^{2+}(d^9)$ state.[9] For it, the failure to see copper-related ODEPR can be explained if the rate limiting process is the hole capture by nonparamagnetic $Cu^{1+}(d^{10})$, which is not spin dependent. Similarly, the failure to see it in the 6885 cm^{-1} bands does not, by itself, disprove the involvement of copper—only that they also do not involve rate limiting carrier capture by Cu^{2+} in its ground state.

The observation of the V^{2+} ODEPR signal in and only in the 6885 cm^{-1} set of lines comes as a surprise. When one actually sees an ODEPR signal in a PL band, it clearly means that the defect giving rise to the ODEPR is involved in a spin-dependent process that is somehow involved in the PL. It could be directly involved in the PL pumping cycle, or in a competing process. Often, as in a process involving simple $S=1/2$ systems, competing processes can be identified with negative ODEPR signals, assisting ones with positive ones. Here, however, the spectra have both positive and negative

components, some of which change sign vs orientation. This often occurs for $S>1/2$ systems, and clouds the issue concerning the assisting or competing role.

Competing processes often show up in more than one PL band. This appears to be the case for the $S=1/2$ X spectrum, which is, for most magnetic field orientations,[11] negative (*competing*) in the 6885 cm^{-1} bands but weakly positive (*assisting*) in the visible PL. V^{2+}, on the other hand, is observed only in the 6885 cm^{-1} bands. This strongly suggests (but does not prove) that it is involved directly in the pumping cycle for them.

We therefore tentatively propose the following process:

$$V^{2+}(d^3) + h^+ \rightarrow [V^{3+}(d^2)]^* \rightarrow V^{3+}(d^2) + h\nu, \qquad (2)$$
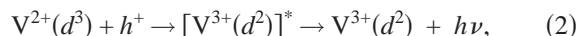
where the spin-dependent process is hole capture by V^{2+} to produce an excited state of the $V^{3+}(d^2)$ configuration, which in its transition to its ground configuration emits the 6885 cm^{-1} PL lines. There are several facts which suggest that this may be reasonable: (1) Both V^{2+} and V^{3+} are known to have stable states in the gap, their EPR having both been observed in ZnO.[10] (2) $V^{3+}(d^2)$ is the electron/hole analog of $Cu^{3+}(d^8)$, and the success in modeling the 6885 cm^{-1} PL spectra as arising from internal transitions for $Cu^{3+}(d^8)$ suggests a similar possibility for $V^{3+}(d^2)$. (3) As pointed out in the introduction, the lines have been reported in many samples which were not intentionally doped with copper.[4] (4) The failure to observe the ODEPR in the 6885 cm^{-1} PL lines for visible excitation, which still effectively produces the PL lines, can reflect the fact that direct excitation of $[V^{3+}(d^2)]^*$ remains possible, even though holes are not being effectively generated for the spin-dependent first step of Eq. (2).

It is interesting to note a similar surprise found in GaN,[12] where an *assisting* (positive) ODEPR signal of $Cu^{2+}(d^9)$ was found in a near-IR PL band which was believed from previous optical studies to arise from an internal transition in V^{3+},[13,14] just the reverse of the $Cu \rightleftarrows V$ roles here. In the GaN case, the spin-dependent process was identified as hole capture by Cu^{2+}, providing again the possibility of confusion between internal transitions of $Cu^{3+}(d^8)$ and $V^{3+}(d^2)$. This was pointed out in the paper, but, in that case, there appeared a way out of the dilemma because in the GaN lattice, Cu^{2+} is negatively charged. This allowed retaining the vanadium identification if the hole captured by Cu^{2+} were to go into an excited shallow effective mass state with lifetime long enough to hop from one such state to another and finally arrive at a V^{2+}. The process would then proceed according to Eq. (2) above, and that was the final interpretation in the paper. In the present case of ZnO, this alternative does not appear possible because V^{2+} is neutral and no shallow hole (or electron) EM state should exist.

IV. SUMMARY

The primary purpose of this brief report has been to report the ODEPR detection of V^{2+} involvement in the 6885 cm^{-1} near-IR bands observed in ZnO, which have universally been assumed to involve copper. They still may involve copper. We cannot rule it out. However, we have tentatively sug-

gested an alternative model, which provides a simple explanation for the ODEPR results, explaining the PL as arising instead directly from vanadium, as a trace unintentional impurity common in ZnO.[6] We hope this stimulates renewed interest in the bands, from both theorists and experimentalists, to properly explain these unexpected results.

We have pointed out also a similar $Cu \rightleftarrows V$ confusion previously observed in GaN, where the roles of the two impurities are reversed. The results here in ZnO, which are not so easily explained away as involving both impurities, suggest that perhaps the identification of the impurity involved in the GaN PL should also be reexamined.

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