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EL2 IN GaAs: PRESENT STATUS

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Even after a decade of intense investigation, the microscopic nature of EL2 is still controversial. Two models must still be considered seriously, namely that EL2 is the isolated As_{Ga} antisite, and that EL2 also contains an arsenic interstitial on the (111) axis. This paper will comment on experiments used to support each of the two models, and will discuss attempts to reconcile the two.

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1. Introduction

What is the structure of EL2? There is evidence that EL2 is the isolated antisite. There is also evidence that it is not the isolated antisite, that it is a *pair* of defects, the antisite plus an arsenic interstitial along the (111) axis. Both cannot be correct, yet at this time, nothing invalidates certain experiments that rigidly support one or the other model. In this paper, we review some experiments and attempt to show that some of them provide a support softer than has been claimed. However, there are still some experiments that conflict with each other and which cannot be easily explained away.

2. Probes of the symmetry

Even before there were specific microscopic models of EL2, there were efforts to probe its symmetry. Unfortunately, interpretations of many of the experiments are ambiguous. There are questions on the limit of sensitivity or else there are uncertainties about what else happens while the experiment is taking place. Some of these were recognized by the original workers; others have been recognized only in retrospect.

2.1. Ballistic phonons

Phonons launched from one face of a sample and detected on the other face have velocities which depend on the symmetry of the phonon. The symmetry of an individual phonon can be recognized by measuring its arrival time after launching a sharply defined pulse. Phonons of a definite symmetry are scattered only if certain selection rules, dependent on the symmetry of the scattering defect, are satisfied.

An experiment performed by Culbertson et al. [1] was to measure the transmission of ballistic phonons through a sample containing EL2. The EL2 was optically and thermally cycled between its ground and metastable configurations. They found that conversion of EL2 from the ground state to the metastable reduced the scattering from defects with C_{3v} symmetry, implying that this was the symmetry of the EL2 ground state. This is compatible with the (111) pair model but not with an isolated antisite.

The authors pointed out that the ionized EL2 concentration in their samples was about equal to that of the neutral EL2. This implies that the number of acceptors which must capture a hole for the EL2 to transfer to the metastable state is about half the number of EL2 present. The caveat in this work, as stated by the authors, is that there is no guarantee that the changes in the ballistic phonon transmission come from changes in EL2, rather than from the changes in the acceptors. Still, unless we assume that the acceptors also undergo large changes in configuration upon hole capture, this caveat would seem to be weak indeed.

2.2. Photoquenching cross-section

Levinson and Kafalas studied transient photocapacitance but they added two new features: polarized light was used and uniaxial stress was applied [2]. They found that the initial rapid transient rise (ascribed to photoionization of the defect) was independent of the directions of both the polarization and stress, but that the slower transient fall (which arose from the transfer of EL2 to its metastable state) depended on the relative orientation of the two external probes. Two kinds of experiments were performed. In the first, stress was applied at low temperature, and then photocapacitance transients were recorded. In the second, stress was applied at high temperature, the sample was cooled, and the stress removed before the photocapacitance transients were recorded at lower temperatures still. The results of these experiments were interpreted as indicating that, while the photoionization took place within a defect of T_d symmetry, the metastable transition involved a pair of defects whose orientation was influenced by the uniaxial stress, at least at temperatures warm enough to allow the pair to reorient. This interpretation has been frequently taken as support for the pair model.

These results can also be understood on the basis of the isolated antisite model, at least as it has been developed in the calculations of Dabrowski and Scheffler [3]. From these, it is clear that the polarization of the light absorbed in the $A_1 \rightarrow T_2$ transition determines which of the three T_2 states will be occupied, and that this in turn determines which of the equivalent (111) directions will be lowered by the Jahn–Teller effect, i.e., the polarization of the light determines the direction the As_{Ga} atom moves in the transition to the metastable. Uniaxial stress along, or perpendicular to that direction will influence the transition rate.

The only aspect of the Levinson and Kafalas experiment that is not explained by this is the persistent influence of stress, applied at high temperatures but released at low temperature before the optical experiment. In the original interpretation, this was taken as evidence that the alignment of the pair was frozen in. In the alternative interpretation, it suggests that the strain is frozen in. At present, there is no way to decide which interpretation is correct.

2.3. Emission rates

Dobaczewski reported a study of emission rates of the EL2 and other defects in GaAs, measuring them as a function of electric field strength for various orientations of the electric field [4]. He reported that EL2 showed a dependence which was different when the electric field was in the (–1–1–1) direction, and asserted that this showed that the defect had an axial structure. Although this result too has been quoted as support for the pair model, it is not at all clear why a defect with full T_d symmetry cannot have different responses to an electric field in different non-equivalent directions, such as (100), (110), (111) etc. This doubt weakens the argument that the anisotropic emission rate proves that EL2 has an axial structure.

2.4. Zero phonon line

The work on the stress splitting of the zero phonon line (ZPL) [5] is well known. From 1984 until 1988, it provided the only solid reason for believing that EL2 was the isolated antisite. This was a time in which the experimental evidence for the pair model was constantly being strengthened. For this reason, an independent confirmation of the stress splitting results was called for, and finally was provided by Bergman et al. [6] and by Trautman et al. [7]. Although both of these workers reported that the original experiments had misidentified a crystal axis, this had no effect on the overall interpretation of the original experiment; the transition being split was an $A_1 \rightarrow T_2$ transition taking place in a system of overall T_d symmetry. There was no room for the interstitial atom in such a symmetry.

Recent developments that weaken the case for using the ZPL stress splitting to determine the symmetry of the defect will be presented in Sec. 3.3.

2.5. Luminescence

Clear and precise symmetry information was obtained from photoluminescence experiments performed by Nissen et al. [8, 9] using a new Fourier photoluminescence technique. The optical transition involved here in the luminescence is quite different from that of the ZPL seen in absorption. Here, an electron at the bottom of the conduction band can fall back onto the unoccupied A_1 midgap level of As_{Ga}, or at low enough temperatures, it can be captured into the lowest effective-mass state (attached to the Γ conduction band minimum) and from there, fall back onto the unoccupied A_1 midgap level. Lattice relaxation gives a no-phonon line and associated replicas. There is experimental evidence that the effective-mass state has A_1 symmetry, because the LO phonon replica is by far the strongest feature in the spectrum, while the zero phonon line is very weak. (An optically forbidden $A_1 \rightarrow A_1$ transition needs a phonon of T_2 symmetry to enable the transition to occur.)

Nissen et al. specifically studied the effect of uniaxial stress on this exceedingly sharp transition. They found no splitting of the transition under uniaxial stress, indicating that there was no orientational degeneracy to be lifted, and correspondingly, that there could be no defect closely attached to the As_{Ga}. At the present time, this can be regarded as the firmest experiment supporting the isolated As_{Ga} model.

2.6. The magnetic resonance experiments

The microscopically structure sensitive ODENDOR experiments reported by the Paderborn group also provide a detailed look at the environment of EL2. In all but their very earliest work [10, 11], they report the presence of an As_i on the (111) axis, giving an overall C_{3v} symmetry and, additionally, a C_{3v} distortion of the neighboring atoms [12]. Although the identification of the position and identity of a particular atom is a process which requires careful analysis of the wave function (and is subject to possible error from using poor model wave functions), it is difficult to understand how the reported C_{3v} symmetry could be in error. The ENDOR work must therefore be regarded as one of the most rigid supporting the pair model.

In their magnetic circular dichroism (MCD) work, the Paderborn group reports two types of signal, one whose shape is like the derivative of a Gaussian broadened line, the other whose shape is more complicated. This latter resembles the derivative of *two* Gaussian broadened lines superposed such that the positive-going peak of one falls on and weakens the negative-going peak of the other. This results in a three peaked structure. The single derivative shape is what one would expect from an discrete A_1 to a nearly discrete T_2 transition, such as the isolated As_{Ga} should exhibit when an electron is ionized from the defect into the conduction band. The defect giving rise to this spectrum is found only in freshly electron-irradiated material. The spectrum is not quenchable as is EL2. When the sample is warmed after irradiation, then the simple MCD signal transforms into the more complex one, a signal which is quenchable like EL2. This is interpreted as happening because the As_{Ga}, which is not EL2, captures some other mobile defect, and becomes EL2.

The weakest part of the interpretation is whether the simple MCD spectrum really corresponds to the isolated As_{Ga} while the more complicated spectrum corresponds to a pair of defects. A calculation by Kaufmann and Windscheif [13] showed the hole transition for the simple isolated As_{Ga} gives rise to the more complicated three peaked MCD spectrum, but that calculation has been criticized and redone by Lannoo et al. [14]. They found that the isolated As_{Ga} had a hole MCD spectrum much weaker than the electron MCD spectrum, and that this latter indeed had the simple derivative shape.

3. Attempts to reconcile conflicting observations

3.1. Quenchable versus unquenchable EL2

One of the early arguments supporting the pair model was that there existed both quenchable and unquenchable forms of EL2, at least as seen by EPR. However, in order for the EPR active form of EL2 to transform to the metastable state, two photons must be absorbed [15]. The first photon converts the EPR-active As^{+}_{Ga}

to As_{Ga}^0 and the second photon causes the $A_1 \rightarrow T_2$ transition of As_{Ga}^0. Clearly, the second photon must be absorbed before As_{Ga}^0 has had time to revert to As_{Ga}^+. Any defect which shortens the lifetime of the electron (e.g., a nearby low lying unoccupied acceptor) will inhibit the transfer of EL2 to the metastable state. One way the existence of a quenchable form of EL2 and a non-quenchable form can be reconciled *without invoking two inherently different structures for the defect* is to consider the effect of the environment on the defect: acceptors, near to some but not all of the As_{Ga}, would shorten the lifetime for those that they were near, rendering them non-quenchable, even though those acceptors were not really a part of the defect structurally.

Possible support for this point of view is provided by EPR measurements of Hoinkis and Weber [16]. They were able to distinguish among various As_{Ga} related defects on the basis of their spin–lattice relaxation time T. Defects with long T were easier to transform to the metastable state, and there was good correlation between short T and inability to quench the EPR spectrum. The authors regarded the short T as being produced by dislocations, clusters of defects and strain fields nearby. Such defects might provide the mechanism by which the electron is removed from the As_{Ga}^0 as well. These experiments confirmed, in a continuous way, earlier observations that, although plastic deformation does increase the amount of As_{Ga} present (as measured by the intensity of the EPR spectrum), it does not increase the amount of EL2 present (as measured by the *quenchable* part of the EPR spectrum [17]).

However, it must be mentioned that the Paderborn group's MCD data disagrees with the point of view expressed above. The shape of their MCD spectrum is different for the quenchable and unquenchable defects. It is the unquenchable defect, whose ODENDOR spectrum shows it to have T_d symmetry, that gives the simpler spectrum expected of the isolated As_{Ga}. The quenchable defects have an ODENDOR spectrum exhibiting C_{3v} symmetry and also have an MCD spectrum which is complicated enough to suggest the presence of something else nearby [18].

3.2. Detection of symmetry lowering

The first attempt to explain the failure of the ZPL stress splitting to see the As_i was that the stress splitting experiments were simply not sensitive enough. The argument was essentially as follows: The As_i, at about two bond lengths distance from the As_{Ga}, provides an environment of C_{3v} symmetry for the As_{Ga} instead of the full T_d symmetry environment that the isolated As_{Ga} would have had. However, the C_{3v} perturbation to the T_d environment might be so weak that, from the viewpoint of stress splitting, it might be overlooked entirely.

The question is thus a quantitative one: how strong is the C_{3v} component of the potential, and what would its effect on the stress splitting be? Calculations to answer this question were carried out [19]. These showed that if the As_i carries a charge of +1, as was demanded by the ODENDOR spectra, and was at a distance comparable to what the ODENDOR spectra suggested, then the Coulomb component of the C_{3v} potential would induce splittings far larger than those actually detected in the optical experiments. Consequently, the stress splitting could not have missed the presence of an interstitial *with properties that the ODENDOR experiments claimed it had.* These calculations, it must be noted, were carried out on the assumption that the stress-split line was actually the ZPL arising from lattice relaxation of the compact T_2 state.

3.3. The ZPL identity issue

A different line of argument to explain the failure of the ZPL results to detect the As_i was initiated by Skowronski [20]. He suggested that the fine structure observed in optical absorption and attributed to the ZPL and its replicas were not phonon lines at all but was rather the spectrum of hydrogenic effective-mass states. Such a spectrum is expected because the Coulomb potential creates an electronic effective-mass state below each conduction band valley. These valley related states then mix under the influence of the crystal potential to give eigenstates of the correct symmetries. Skowronski noted that the experimental final state energy of an electron undergoing the 1.04 eV $A_1 \rightarrow T_2$ "ZPL" transition is immediately below the L band minimum. He suggested that each of the four L band minima would give rise to a hydrogenic wave function, that the T_d symmetry of the crystal as a whole would cause the eigenstates of the system to be A_1 and T_2 linear combinations of these four, and that the optical transition from the deep lying A_1 initial state would see only the T_2 final state. Such a scenario, all of whose features are very reasonable, would account in a natural way for the exceedingly small splitting of the final state when the stress was along a (100) direction.

The main thrust of the argument, however, is that if the final state were a hydrogenic state of large radius (instead of being the ZPL of the compact T_2 state), it would not sense the symmetry lowering caused by an atom very close to the central As_{Ga}. Thus, the optical absorption would no longer be a sensitive probe of the microscopic structure of EL2, and EL2 could indeed be the pair as revealed by the magnetic resonance experiments, even though the uniaxial stress indicated a defect of T_d symmetry.

The pressure experiments of Baj and Dreszer [21] again raised the identity issue for the ZPL because they showed that, under pressure, the "ZPL" moved up onto the flanks of the broad absorption peak. (A zero phonon line must mark the endpoint of a broad transition if lattice relaxation is the cause of the broadening.) These experiments also provided data on the hydrostatic pressure dependence of the ZPL energy. Von Bardeleben and Bourgoin noticed that the pressure dependence of the ZPL transition was such that its final state exactly tracked the L band minimum under hydrostatic pressure [22]. This provided an additional piece of data supporting Skowronski's hypothesis. The impact of this idea was substantially weakened by the fact that it was embedded in papers which proposed a radical theory of the EL2 metastability, a theory based on the existence of an A_1 effective-mass state lying *below* the T_2 effective-mass states [23]. This was at variance with the observed sign of the non-linear effects in the stress splitting, which shows that the unobserved A_1 state must lie *above* the T_2.

The most recent development in this argument was provided by Lannoo et al. [14]. They showed that for a deep donor, the arguments which lead to the conventional T_2 above A_1 ordering are in fact reversed: the correct order should be A_1 above T_2 for the effective-mass-like states. They showed, moreover, that the Hamiltonian for the states derived from the L band minima is identical in form with that used for the dynamic Jahn–Teller analysis of the zero phonon line. This means that any aspect of the 1.04 eV absorption that can be explained on the assumption that it is the ZPL can be explained equally well on the assumption that it is the transition to the L band T_2 hydrogenic state. An argument favoring the effective-mass explanation is that *three* measured properties of the 1.04 eV absorption feature (namely, its energy, its hydrostatic pressure dependence, and the linear part of its stress splitting), are fit by a Hamiltonian whose parameters, while arbitrary from the ZPL point of view, are obtained from the known properties of the L band in bulk GaAs. There is an additional piece of experimental evidence supporting the hydrogenic interpretation: Spaeth and Krambrock [24] have found basically the same ZPL and phonon replica structure on another defect (i.e., at a different photon energy which corresponds to a different initial energy for the transition but the same final energy). This suggests that the structure in the absorption is not tied closely to the microscopic structure of the defect.

4. Conclusion: open problems

Over the last decade, the consensus opinion on the structure of EL2 has undergone shifts. During the first part of that period, although stress splitting of the ZPL indicated that EL2 was the isolated As_{Ga}, this was not accepted by much of the defect community, for several reasons. First of all, there was a belief that the isolated As_{Ga} could not exhibit large lattice relaxation of the sort needed for metastability: it was not associated with especially weak bonds, such as would be found at a vacancy or an interstitial. Secondly, some workers felt that the analysis of the non-linear aspects of the stress splitting was suspect, that having to invoke the coupling to the lattice via the dynamic Jahn–Teller effect was an admission that something was wrong. Finally, the alternative idea that EL2 also contained an arsenic interstitial, an atom that *was* expected to move, was supported by many direct and indirect experiments.

The situation changed when the calculations of Dabrowski and Scheffler showed that metastability of the isolated As_{Ga} could occur, and that many of the properties of EL2 arise very naturally from their calculated CC diagram. Calculations of other types appeared: these supported the original stress splitting analyses and reaffirmed the ability of the stress-split ZPL to detect the nearby As_i. The stress-splitting experiments themselves were repeated and the original results reconfirmed. At the same time, however, the findings of the Paderborn group, that the As_i is always seen in the quenchable defect, did not go away. In fact, their further experiments on the transformation of the simple quenchable MCD spectrum into the complex quenchable one has added credence to the As_{Ga}–As_i pair model. Older calculations [25] were not able to reconcile the calculated properties of EL2 with the pair model as proposed in Ref. [12]. Recent calculations [26, 27] have not been able to reconcile the calculated properties of EL2 with the newer version of the pair model proposed in Ref. [24].

At present, confidence that the ZPL is actually able to detect the presence of the As_i has been (perhaps fatally) weakened by the possibility that the so-called ZPL is, instead, the transition to hydrogenic states. The major challenge to the pair model from that source has disappeared. Ironically, just when it did disappear, a new challenge to the pair model replaced it, this one coming from the highly precise photoluminescence work. There is no reason to doubt either the findings of the Paderborn group or the photoluminescence data: Yet, as they are presently interpreted, they cannot both be correct. At the time of this writing, there is ongoing work, both experimental and theoretical, to clarify the interpretations of these seemingly irreconcilable experiments.

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