Stress Splitting of the $A_1 \rightarrow T_2$ Transition of As_{Ga}: Implied Absence of As_i in the Structure of $EL2$

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We have calculated the stress splitting of the $A_1 \rightarrow T_2$ optical transition of the neutral As_{Ga} in the presence of two perturbations, each of which is small compared to the Jahn-Teller relaxation energy. These are (i) a nearby As_i such as has been postulated to be a component of $EL2$, and (ii) the kinetic energy of the As_{Ga}. The presence of the As_i causes the calculated splitting to be incompatible with what has been observed by Kaminska, Skowronski, and Kuszko. To the extent that those observations have been linked to $EL2$ by other experiments, this calculation rules out the As_i as a component of $EL2$.

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There are presently two microscopic models of $EL2$ (an important metastable native defect in GaAs) which have reasonable experimental and theoretical support. One is that $EL2$ is simply As_{Ga}, the isolated arsenic antisite.[1-4] The other is that $EL2$ is a loosely bound As_{Ga}-As_i pair, where the As_i (the arsenic interstitial) lies along a [111] antibonding direction, at about $1\frac{1}{2}$ bond lengths from the As_{Ga}.[5-7] There are many experiments *consistent* with one or the other of the two models;[8] none of these bears so directly on the question of microscopic structure as do those cited above. Of these, the experiment that most directly identifies $EL2$ with the isolated As_{Ga} is that of Kaminska, Skowronski, and Kuszko[1] who measured the stress splitting of the zero-phonon line in an $A_1 \rightarrow T_2$ optical transition. On the other hand, the experiments that most directly assert the presence of the As_i on the [111] axis are the optically detected electron-nuclear double-resonance (ODENDOR) measurements by Meyer *et al.*[6,7]

The purpose of this Letter is to demonstrate that the presence of the As_i at the location specified by the ODENDOR measurements[6] is incompatible with the stress-splitting experiments. We show that the As_i should have been detected by its effect on optical transitions at the As_{Ga}. The argument in a nutshell is as follows: Electronic structure calculations for the As_i-As_{Ga} pair,[9] assuming that the pair *is* $EL2$, predict a $1+$ charge for the As_i. (This happens to be in agreement with the way the ODENDOR results have been interpreted.[6]) The electronic matrix elements of the As_i Coulomb potential, taken with respect to the final T_2 states of the As_{Ga}, are large compared to those of the stress. The effect of the Coulomb potential is substantially larger than the resolution of the stress experiments. It therefore would not have been missed.

Although I have suggested this argument earlier,[10] the earlier suggestion was incomplete in that it neglected the Jahn-Teller effect.[11] The energy of Jahn-Teller relaxation is much larger than either the Coulomb splittings or the stress splittings. Under these conditions, it might quench the final-state Coulomb splitting to an unobservably small value, as it quenches many other observables. The proper way to study the problem is to include the Jahn-Teller coupling in zeroth order, and then add the Coulomb potential of the As_i to a Hamiltonian appropriate to strong Jahn-Teller coupling. This we do and show that the resulting pattern of stress splittings is incompatible with what was observed.[1]

The derivation of the Hamiltonian to describe this system is too lengthy to present here. The underlying physics, however, is simple to describe and the technique of translating it into an effective Hamiltonian can be learned by studying Ref. 11. The starting point is the observation that local-density pseudopotential calculations[3] show that the energies of the electronic states centered on the As_{Ga} depend strongly on its displacement from the gallium site. When the As_{Ga} moves, there are lesser displacements of the four nearest-neighbor atoms and so on, but their effect on the energies of the states is correspondingly less. We simplify this by taking the displacement of the As_{Ga} as the only lattice coordinate that couples to the electronic energies. The same calculations[3] show that after an $A_1 \rightarrow T_2$ optical transition, the As_{Ga} relaxes to a relative energy minimum (the Jahn-Teller minimum) at a displacement of about 0.25 Å from the gallium site, and lowers its energy thereby by about 0.12 eV. Over this range of displacements, the electronic eigenvalues are reasonably linear in displacement and the total energy is reasonably quadratic. This justifies expanding the electron-lattice interaction to linear order and the lattice potential to quadratic order. In doing so, applying the condition that the overall Hamiltonian be invariant under the point group T_d (the symmetry of the As_{Ga}) and retaining only the matrix elements in a single T_2 manifold (that of the final state of the neutral As_{Ga}) results in the familiar $T_2 \times \tau$ Hamiltonian.[12,13] Not all the steps in the above procedure can be firmly justified; the strengths and weaknesses inherent in proceeding in this way will be discussed fully elsewhere.[14] The weakest point in the derivation is that the T_2 final state is not a discrete state; it is merely a well-defined resonance low in the conduction band.

In the situation of interest here, the system is strongly coupled in the usual Jahn-Teller sense. The appropriate basis to use in solving this Hamiltonian is a vibronic basis: Each basis state is the product of a three-dimensional lattice harmonic oscillator (centered at a Jahn-Teller minimum) with the corresponding electronic state. The latter is the lowest electronic state when the As_{Ga} sits in the Jahn-Teller minimum. There are four vibronic states, one for each of the equivalent Jahn-Teller minima into which the As_{Ga} can relax. Linear combinations of these four can be chosen which transform under T_d like S (i.e., A_1), X, Y, and Z (i.e., partners of T_2). These four, in that order, define the basis set we use below.

In this basis, and with a suitable zero of energy, the matrix of the $T_2\times\tau$ Hamiltonian has only one nonvanishing element. Its value is denoted as 4Γ, where Γ is the overlap matrix element of the Hamiltonian between any two original vibronic states. We denote the three stress directions of interest, namely, $\sigma\|[100]$, $\sigma\|[110]$, and $\sigma\|[111]$, by $j=1$, 2, and 3, respectively. The three matrices representing the stress, Σ_j, in the S,X,Y,Z basis can be written as[14]

$$\Sigma_1=\sigma V_0 I_4+\sigma V_1\begin{pmatrix}0&0&0&0\\0&2&0&0\\0&0&-1&0\\0&0&0&-1\end{pmatrix}, \tag{1a}$$

$$\Sigma_2=\sigma V_0 I_4+(\sigma/2)\begin{pmatrix}0&0&0&V_2\\0&V_1&V_2&0\\0&V_2&V_1&0\\V_2&0&0&-2V_1\end{pmatrix}, \tag{1b}$$

$$\Sigma_3=\sigma V_0 I_4+(\sigma V_2/3)\begin{pmatrix}0&1&1&1\\1&0&1&1\\1&1&0&1\\1&1&1&0\end{pmatrix}, \tag{1c}$$

where $V_0\equiv\frac{1}{3}S^{A_1}$, $V_1=\frac{1}{3}K^E S^E$, and $V_2=K^{T_2}S^{T_2}$. The S^Γ ($\Gamma=A_1$, E, and T_2) are constants which describe the stress coupling in the purely electronic basis $|x\rangle$, $|y\rangle$, and $|z\rangle$. K^E and K^{T_2} are Ham reduction factors[11] and I_4 is the 4×4 unit matrix.

Consider next the matrix elements of the potential caused by the As_i at the site suggested by the ODENDOR experiments: There are four such sites, one along each antibonding direction. We use i to label a specific site according to the scheme depicted in Fig. 1. Each of the four arsenic atoms is given a number, $i=1$-4. The interstitial site i is taken to be on the same axis as neighbor i. The matrix H_i is the sum of the $T_2\times\tau$ Hamiltonian (describing the isolated As_{Ga}) and the potential v_i arising from the interstitial at position i. We can show[14]

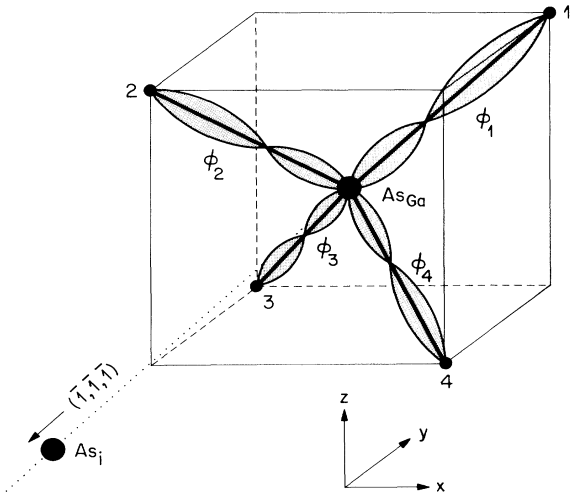

FIG. 1. Diagram of the vicinity of the As_{Ga}, showing its four nearest neighbors, numbered 1,2,3,4, and, on the axis through neighbor 1, an arsenic interstitial in the antibonding direction at $1\frac{1}{2}$ bond lengths from the antisite.

that

$$H_i=\begin{pmatrix}4\Gamma+u & M_x^i v & M_y^i v & M_z^i v\\ M_x^i v & u & M_z^i v & M_y^i v\\ M_y^i v & M_z^i v & u & M_x^i v\\ M_z^i v & M_y^i v & M_x^i v & u\end{pmatrix}, \tag{2}$$

where $u=a/2\sqrt{3}$ and $v=K^{T_2}\tau/2\sqrt{2}=\tau/3\sqrt{2}$. The integers M_μ^i appearing in Eq. (2) are ±1, and are described by saying that neighbor i lies along the $[M_x^i,M_y^i,M_z^i]$ bonding direction. a and τ are defined by the following prescription:[14] We form those linear combinations of the four potentials v_i which transform according to A_1 and T_2, namely, $v^{A_1}=\frac{1}{2}(v_1+v_2+v_3+v_4)$, $v_x^{T_2}=\frac{1}{2}(v_1-v_2-v_3+v_4)$, etc. Then the matrix elements of these potentials in the purely electronic basis $|x\rangle$, $|y\rangle$, $|z\rangle$ are written as

$$\langle\mu|v^{A_1}|\nu\rangle=a\theta_{\mu\nu}^{A_1},\quad \mu,\nu=x,y,z, \tag{3a}$$

$$\langle\mu|v_j^{T_2}|\nu\rangle=\tau\theta_{\mu\nu}^{T_2}(j),\quad j=x,y,z, \tag{3b}$$

where the θ^{A_1} and $\theta^{T_2}(j)$ matrices are the group coupling coefficients[15] for $[T_2\times T_2]=A_1+E+T_2$, arranged in matrix form, namely, $\theta_{\mu\nu}^{A_1}=(1/\sqrt{3})\delta_{\mu\nu}$ and

$$\theta_{\mu\nu}^{T_2}(j)=(1/\sqrt{2})(1-\delta_{\mu\nu})(1-\delta_{\mu j})(1-\delta_{\nu j}).$$

This defines a and τ.

A rough estimate of a and τ will suffice because the relevant question is whether or not the crystal-field splitting caused by v_i is large compared to the stress splittings. Therefore, we regard the $|x\rangle$, $|y\rangle$, and $|z\rangle$ states as linear combinations of the four antibonding orbitals

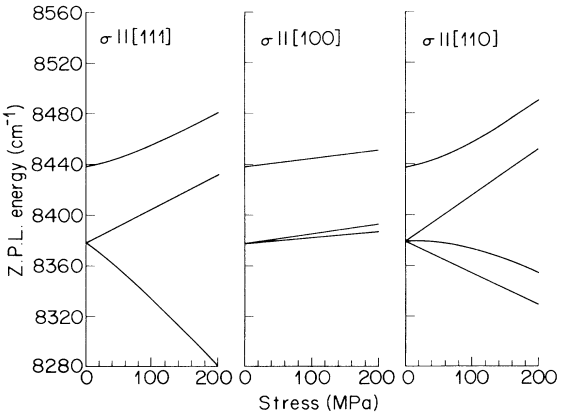

FIG. 2. Plot of the eigenvalues of the 4×4 Hamiltonian for the isolated As_{Ga} acted upon by uniaxial stress. The parameters chosen are those used by Kaminska, Skowronski, and Kuszko (Ref. 1) and the results agree with their theoretical expressions.

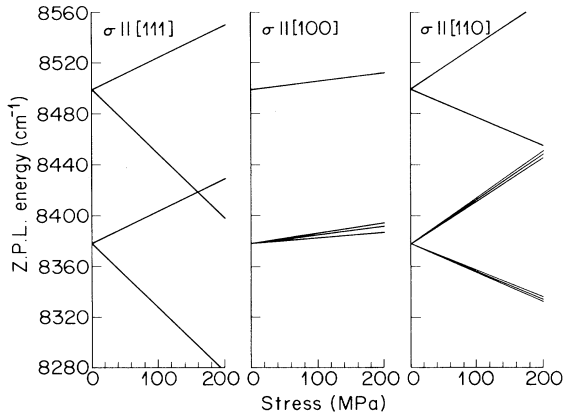

FIG. 3. Plot of the eigenvalues of the 4×4 Hamiltonian for the As_{Ga}-As_i pair acted upon by uniaxial stress. The parameters V_0, V_1, and V_2 are close to those used in Fig. 2, and chosen so as to make the lines which go to 8378 cm^{-1} correct for $\sigma\|[100]$ and $\sigma\|[111]$. We use $\tau=0.016$ eV and $\Gamma=0$. Note that the $\sigma\|[110]$ spectrum is unlike that of Fig. 2, which accurately reproduces the experimental data.

sketched in Fig. 1. The justification for doing so comes from a study of the form of the states as revealed by pseudopotential calculations. The potential about the charged As_i takes the form $-e^2/\epsilon r$ at large distances. Appreciable deviations occur only for $r<b$, where b is the bond length. Thus, the four orbitals shown in Fig. 1 experience the long-range potential $-e^2/\epsilon r$. The expectation value of v_1 with respect to any of the ϕ_j orbitals can be written as $\langle v\rangle_j \approx -e^2/\epsilon r_j$, where r_j is the distance from the As_i on the $i=1$ axis to the charge center of orbital ϕ_j. A reasonable estimate of the location of the charge center for orbital ϕ_j, based on pseudopotential calculation of the charge density of various states, is midway between the As_{Ga} and the nearest neighbor j. The As_i is at $1\frac{1}{2}$ bond lengths from the As_{Ga}, so $r_1=2b$, $r_2=r_3=r_4=b\sqrt{2}$, where $b=2.45$ Å, the bond length in GaAs, and $\epsilon=12.8$. Using these values, $\langle v\rangle_1=-0.23$ eV and $\langle v\rangle_2=\langle v\rangle_3=\langle v\rangle_4=-0.32$ eV. The spatial separation between the orbitals ϕ_i is so great that we can ignore matrix elements between different orbitals ϕ_i and ϕ_j in comparison to those between the same orbitals. This gives $\alpha=-1.03$ eV and $\tau=0.064$ eV.

The argument to be made is that τ is large enough to alter the stress-splitting pattern. To be safe in making this argument, we mention one effect which might reduce the values just obtained, namely, that the As_{Ga} is more polarizable than the perfect crystal. This is because of the smaller energy difference between occupied and unoccupied electronic states. However, it is not reasonable to expect more than a factor of 4 reduction arising from this cause,[14] and even that factor is extremely conservative. Even with the full factor of 4 reduction, $\tau=0.016$ eV is large compared to the energies of the stress splittings.

The Hamiltonian which describes the As_{Ga} with the interstitial along the $i=1,\ldots,4$ antibonding axis and the stress along the $j=1,\ldots,3$ direction is $H(i,j)\equiv H_i+\Sigma_j$. The observed spectrum for any stress direction j is the sum of all spectra for axes $i=1,2,3,4$ weighted equally, with the intensity of any line $E_n(i,j)$ weighted by the appropriate optical transition matrix elements.

If we now consider the isolated As_{Ga}, i.e., if we set $\alpha=0$ and $\tau=0$, the resulting Hamiltonian can be diagonalized analytically.[1,14] The results are plotted in Fig. 2, using the same parameters as chosen in Ref. 1, namely, $4\Gamma=60$ cm^{-1}, $V_0,V_1,V_2=0.065,-0.01,-0.61$ cm^{-1}/MPa. We take the energy zero at 8378 cm^{-1} so that these eigenvalues now represent the transition energy from the A_1-symmetry initial state roughly 1.04 eV below. The highest-energy state for each stress is not observed in optical absorption. The other lines in Fig. 2 describe perfectly the stress-splitting experiments of Ref. 1.

Now the question is whether, even with the smallest values of α and τ given here, there is any way to choose the parameters V_0, V_1, V_2, and 4Γ so as to reproduce the part of the spectrum in Fig. 2 that goes to 8378 cm^{-1} at zero stress. The answer is *definitely no*. This comes about for the following reason: The observed stress splitting is described perfectly by those lines which, in Fig. 2, go to 8378 cm^{-1} at zero stress. The other lines, which go to 8438 cm^{-1}, are optically forbidden and are not seen. There is no comparable selection rule when the As_i is present. To explain why these lines are not seen (and they should be as strong as the others) we must assume either that Γ is so small that they are degenerate with the lines that are seen, or that Γ is so large that the lines are up out of the way in the multiphonon continuum. The first possibility leads to spectra of the form shown in Fig. 3. The second leads to spectra of the form shown in

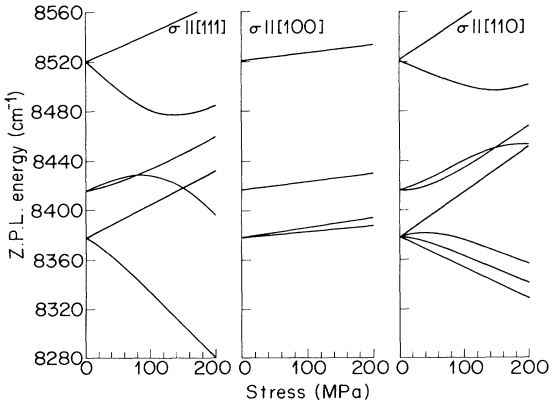

FIG. 4. Same as Fig. 3, but with $\Gamma = 15$ cm^{-1}. The parameter τ controls the zero-stress splitting between the 8520-cm^{-1} line and the 8378-cm^{-1} line; the parameter Γ controls the zero-stress splitting between the 8416-cm^{-1} line and the 8378-cm^{-1} line.

Fig. 4. Once Γ is fixed, V_0 and V_1 can be chosen to make the $\sigma\|[100]$ spectra have the right form, while V_0 and V_2 can be chosen so as to make the $\sigma\|[111]$ spectra have the right form. The last spectrum, $\sigma\|[110]$, is completely determined and as can be seen, it either has the wrong shape (Fig. 3) or an extra line (Fig. 4).

The resolution of the stress-splitting experiments, as inferred from the data in Ref. 1, was of the order of 8 cm^{-1}. Therefore, the spectra as calculated in Figs. 3 and 4 (which are the best we can do), make it highly unlikely that the charged As_i could have escaped detection in the stress-splitting experiments. Since the no-phonon line of the As_{Ga} has been linked to *EL2* (it appears in the optical cross section for excitation to the metastable state[2]) this conclusion would seem to rule out the As_i as a component of *EL2*.

Clearly, there is a tacit assumption here that, having proved that the stress-splitting results and the ODENDOR interpretation are incompatible, we regard the stress-splitting results as being more reliable. We do so for two reasons: First, the stress-splitting experiments have been recently repeated independently and the results have been confirmed.[16] Second, the passage between data and theory is far more direct for the stress-splitting experiments than for the ODENDOR measurements. However, aside from the question of the reliability of the interpretation, we have shown here that the two results are mutually exclusive.

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