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Theoretical Model for Vanadium Doped Gallium Arsenide

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ABSTRACT

An orthorhombic strain model for V^{2+} in GaAs is presented in this work. Spin and effective Hamiltonians are derived for this model. A brief summary of the Jahn-Teller effects and random strains has been given. The JTEs show them selves by introducing reduction factors in the first and second terms of effective Hamilltonian and the random strains by lowering the local symmetry at V^{2+} ion sites.

نموذج نظرية لـ (GaAs) المطعم بالفاناديوم

الملخص

يقدم هذا العمل صياغة لنموذج المطاوعة متعامدة المحاور للفاناديوم V^{2+} في زرنيخات الكاليوم (GaAs). اذ تم اشتقاق مؤثر الطاقة الخاص بالبرم (H_{spin}) ومؤثر الطاقة الفعال (H_{eff}) لهذا النموذج، مع اعطاء نبذة عن تأثير Jahn-Teller وتأثيرات المطاوعة الحاصلة في البلورة المشوبة. ان تأثيرات Jahn - Teller تم التعبير عنها في صياغة النموذج بمعاملات تقليل التفاعلات في الحد الاول والثاني لمؤثر الطاقة الفعال في حين تم التعبير عن تأثيرات المطاوعة بتقليل التناظر الموضعي عند موضع ايون V^{2+}.

INTRODUCTION

One of the agents responsible for this time of change is the semiconducting “chip” which forms the building block of the new generation of electronic devices and computers. Silicon and Germanium were the first semiconductors to be developed but now moves are being made towards III-V compounds such as GaAs, GaP and InP. These materials are becoming increasingly used as integrated circuit substrates in electronic and photoelectronic devices. Gallium arsnide is especially important in view of its use in high frequency electronic and high speed logic circuit (Vittone et al., 1999).

When first confronted, imperfections in semiconducting crystals may seem to be a hindrance to device production. However, when it is realised that completely, pure samples are impossible to grow and that the imperfections dominate the properties of semiconductors, the understanding and control of impurities is vital in device technology. Impurities create electrically important energy levels within the band gap of semiconductor for example, shallow donor or acceptor levels lie close to the band edges and control the n- or p- typeness of the material and its conductivity. On the other hand, deep levels when present in significant concentrations compensate the residual shallow dopants and reduce the free carrier density thus producing semi-insulating, thermally stable material which is invaluable in device fabrication. This latter mechanism is used in GaAs technology.

In 1984 Kutt, (Kutt et al., 1984), suggested that the use of Vanadium could be advantageous. They found that V-doping produced semi-insulating GaAs which was relatively easy to grow and that V diffused by one order of magnitude less than Cr in all cases investigated. These promising results, however, had to be tempered by the fact that the role played by Vanadium was far from clear and its characterisations was far from complete.

Many experimental results obtained by (Vasson et al., 1986). Their thermally detected (TD-)EPR and acoustically detected (AD-)EPR measurements were supplemented by APR experiments perform by (Rampton et al., 1986). These efforts in experimentation called for equal efforts in theoretical modelling. As no suitable model was available, a complexed V^{2+} center, was postulated to account for these results. Theoretical calculations performed by (Katayama-Yoshida and Zunger, 1986) predict a low spin ^2E state in violation of Hund’s rule whilst (Atkinson, 1987) find that the center couples to T_2 modes of distortion only and so propose a $^4T_1$ ground state.

In our analysis, this complex is expected to have a $^4T_1$ ground state which splits into six Kramers doublets with three of them being close together and lying lowest in energy. This assignments is necessary in order to explain the many transition which are observed when the levels are split by a magnetic field. A consequence of the closeness of the energy levels has made the modelling of this centre a difficult problem.

An orthorhombic model is presented in this work for V^{2+}, spin and effective Hamiltonians are derived for this model. The basic theory of Jahn-Teller effects and random strains needs to be explained before the construction of this model.

THEORY

The V^{2+} ion identified in experimental and theoretical works is strongly coupled to the lattice and is therefore subject to static and dynamic distortion of its surroundings. This brings in to play random internal strains and Jahn-Teller effects. These concepts have to be explained before the model for the V^{2+} ion can be proposed.

1. Jahn-Teller Effects:

The electronic energy levels of a paramagnetic impurity ion embedded in a crystal are affected by the host lattice. To a first approximation, the ionic lattice produces a static electric field which interact with the impurity and alters its electronic energy levels and eigen states. Also any orbital degeneracy present in the three ion may be lifted by this crystal field.

However, reality is not so straightforward. The lattice is not rigid and the coupling between the impurity and its vibrating surroundings has to be considered. This ion-lattice coupling give rise to so-called “Jahn-Teller Effects” (JTEs).

Our need in this work is to look at how the coupling shows up. Firstly, the states of the ion are not purely electronic but contain vibrational components. They are known as “vibronic” states. Secondly, a dynamic JTE causes the appearance of reduction factors in front of certain orbital operators and of additional large second-order terms in an effective Hamiltonian.

1.1 JETs in Orbital Triplits:

Suppose a single ion is placed in a crystal. The Hamiltonian for the system has the form:

$$H = H_{ion} + H_{lattice} + H_{ion\text{-}lattice} \tag{1}$$

where

H_{ion} – the Hamiltonian for the free ion and includes the spin-orbit coupling, random strains and Zeeman terms.

$H_{lattice}$ – describes the vibrations of lattice.

$H_{ion\text{-}lattice}$ – the interaction between the ion the lattice vibrations.

We start by making the assumption that the ion-lattice interaction is linear.

Then :

$$H_{ion=lattice} = V_E\,(Q_\theta\,E_\theta + Q_\varepsilon\,E_\varepsilon) \tag{2}$$

where

V_E – the ion-lattice coupling constant.

Q_θ & Q_ε - the e-type collective coordinates which describe the displacements of the nearest neighbour tetrahedron.

E_θ & E_ε - the orbital operators with :

$$\left.\begin{aligned} E_\theta &= \frac{1}{2}\left[3\ell'^2_z - \ell'(\ell'+1)\right] \\ E_\varepsilon &= \frac{\sqrt{3}}{4}\left(\ell'^2_+ + \ell'^2_-\right) \end{aligned}\right\} \tag{3}$$

using an isomorphism of $\ell' = 1$.

The Hamiltonian (H) can be simplified by applying a unitary transformation involving the orbital operators and the lattice momenta (Bates, 1978). This results in $H_{ion\text{-}lattice}$ being replaced by the Jahn-Teller energy - $|E_{JT}|$ and $H_{lattice}$ by the energy of a system of simple harmonic oscillators. Furthermore, if an average is taken over the oscillator ground state, H_{ion} is greatly simplified. As an example suppose H_{ion} consists of spin-orbit coupling only. The transformation gives :

$$H_{ion} = \gamma\lambda k_1^{T_1}\,\underline{\ell'}.\underline{S} + \lambda\{c[S(S+1) + (E_\theta E_\theta^S + E_\varepsilon E_\varepsilon^S)] + b(\underline{\ell'}.\underline{S})^2\} \tag{4}$$

where

γ - the first order Jahn-Teller reduction factor and cause the quenching of the spin-orbit operator , known as Ham effect, (Ham, 1965).

λ- the spin-orbit coupling parameter.

$k_1^{T_1}$ - the isomorphic factor.

$E_\theta^S \equiv E_\theta$ with ℓ - operators replaced by S-operators.

The constants b, c are given by:

$$\left.\begin{aligned} c &= -\frac{2}{3}(k_1^{T_1})\,\lambda\,(F_b - F_a) \\ b &= -(k_1^{T_1})^2\,\lambda\,F_a \end{aligned}\right\} \tag{5}$$

where
F_a and F_b are the second order Jahn-Teller factors.

2. Random Strain:

Consider a crystal containing a substitutional impurity ion at a site of tetrahedral symmetry. The static departure of its neighbours form their ideal lattice positions will effectively reduce the site symmetry from T_d. This is referred to be as “random strain” and is due to other impurities, crystal defects, dislocations and random changes.

2.1 Tetragonal Strains:

These e-type strains are denoted by $\overline{Q}_\theta$ and $\overline{Q}_\varepsilon$. A particular ion can be represented by a point P(ε, ϕ) on a $\overline{Q}_\theta$, $\overline{Q}_\varepsilon$ digram (Fig. 1)

All sites represented by points along the $\overline{Q}_\theta$ axis (ϕ=0) correspond to a tetragonal distortion along [001] axis (O_z). Those sites along $\phi=2\pi/3$ and $\phi=4\pi/3$ directions correspond to tetragonal distortions along the [100] and [010] axes (O_x and O_y) respectively.

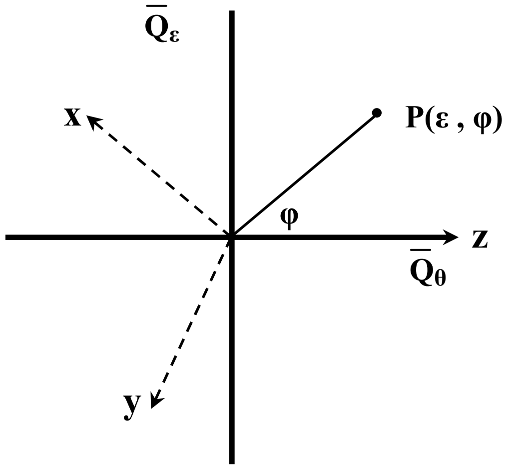

Fig.1 : The $\overline{Q}_\theta - \overline{Q}_\varepsilon$ plane.

The strain distribution function N(ε,ϕ) represents the number of impurity ions (in this work V^{2+}) occupying sites with strains in the range ε to ε+dε and ϕ to ϕ + dϕ (Bates and Stevens, 1986).

2.2. Trigonal Strain:

To describe t_2-type strain, $\overline{Q}_4$, $\overline{Q}_5$ and $\overline{Q}_6$, a three dimensional diagram is needed. A pure trigonal distortion along the [111] axis is represented by

$$\overline{Q}_4 = \overline{Q}_5 = \overline{Q}_6 \tag{6}$$

The other three trigonal distortion along the $[\bar{1}\,\bar{1}\,1]$, $[1\,\bar{1}\,\bar{1}]$ and $[\bar{1}\,1\,\bar{1}]$ axes are obtained when:

$$\left.\begin{aligned} -\overline{Q}_4 &= -\overline{Q}_5 = \overline{Q}_6 \\ \overline{Q}_4 &= -\overline{Q}_5 = -\overline{Q}_6 \\ -\overline{Q}_4 &= \overline{Q}_5 = -\overline{Q}_6 \end{aligned}\right\} \tag{7}$$

respectively.

Finally a strain distribution function for trigonal strains can be defined in a similar way to that for tetragonal strains.

2.3. Orthorhombic Strains:

For a system coupled to one e-mode and one t_2-mode, a five dimensional figure is needed. The pure tetragonal and pure trigonal sites are defined as before but six additional orthorhombic types of site can be identified.

A strain distribution function also exists for orthorhombic strains.

The GaAs : V^{2+} Orthorhombic Strain Model

As the iso-electronic Cr^{3+} ions in GaAs, which give rise to EPR spectra, are known to occupy orthorhombic sites (Krebs and Stauss, 1977), we suppose that the random strains acting on the V^{2+} ions should reflect orthorhombic symmetry.

Taking the ground state of V^{2+} ($3d^3$) ion in T_d symmetry to be $^4T_1$, the following perturbation will be considered (Fig. 2).

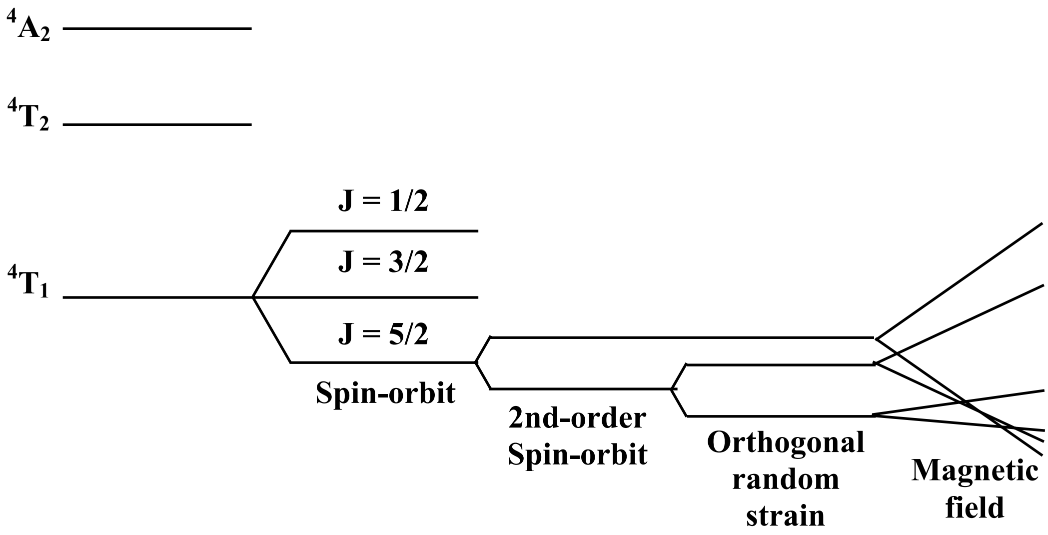

Fig. 2 An energy level scheme for the $^4T_1$ ground state of the V^{2+} ion

1. The Spin Hamiltonian:

The Hamiltonian describing the orthorhombic distortion is given by:

$$H_{strain} = H_D + H_E \tag{8}$$

Where H_D represents the tetragonal random strain along the [001] axis and H_E, the corresponding trigonal random strain . They are written as :

$$\left.\begin{aligned} H_D &= D\{3S'^2_z - S'(S'+1)\} \\ H_E &= \pm E(S'_x S'_y + S'_y S'_x) \end{aligned}\right. \tag{9}$$

The orthorhombic random strain Hamiltonian for two of the six orthorhombic sites is:

$$\left.\begin{aligned} &H_{strain} = D\{3S'^2_z - S'(S'+1)\} \pm E(S'_x S'_y + S'_y S'_x) \\ \text{or}\quad &H_{strain} = D\{3S'^2_z - \frac{35}{4}\} \pm \frac{iE}{2}(S'^2_+ - S'^2_-) \end{aligned}\right\} \tag{10}$$

with cyclic interchange of x, y and z giving the Hamiltonian for the other four sites.

Although H_{strain} has been chosen to have orthorhombic symmetry, it does not imply that we assume that the JTE is of the pure $T \otimes (e+t_2)$ type which pushes the orthorhombic potential minima in Q-space lower in energy than any other potential minima . In stead, we assume that the JTE is of the common $T \otimes e$ type and that the ion is sensitive to both e-and t_2-type cluster displacements such as strain but that the D:E ratio is not restricted (Bates et al., 1987).

To complete the spin Hamiltonian, an A-type term, H_A and the Zeeman interaction Hamiltonian , H_z have to be added. H_A is given by:

$$\left.\begin{aligned} H_A &= A[S'^4_x + S'^4_y + S'^4_z - \frac{1}{5}S'(S'+1)(3S'^2+3S'-1)] \\ \text{or}\quad H_A &= A[\frac{1}{8}(S'^4_+ + S'^4_-) + \frac{7}{4}S'^4_z - \frac{95}{8}S'^2_z + \frac{567}{64}] \end{aligned}\right\} \tag{11}$$

H_z is written as:

$H_z = g\,\beta\,\underline{B}\,.\,\underline{S'}$

or $$H_z = \beta\{g_{\|} B_z S'_z + g_{\perp}(B_x S'_x + B_y S'_y)\} \tag{12}$$

or $$H_z = \beta\{g_{\|} B_z S'_z + \frac{1}{2}[g_{\perp}(B_x + iB_y)S'_- + g_{\perp}(B_x - iB_y)S'_+]\} \tag{13}$$

The spin Hamiltonian is :

$H_{spin} = H_{strain} + H_A + H_z$

or

$$\begin{aligned} H_{spin} = {} & D\{3S'^2_z - S'(S+1)\} \pm E(S'_x S'_y + S'_y S'_x) + \\ & A\{S'^4_x + S'^4_y + S'^4_z - \frac{1}{5}S'(S'+1)(\{3S'^2+3S'-1)\} \\ & + g\,\beta\,\underline{B}\,.\,\underline{S'} \end{aligned} \tag{14}$$

2. The Effective Hamiltonian:

An effective Hamiltonian (H_{eff}), for an ion with a degenerate state ($\ell'=1, S=\frac{3}{2}$) coupled to the vibration of the lattice, may be used to model the behaviour of six Kramers doublets arising from the $^4T_1$ ground state may be written as :

$$H_{eff} = H_{so} + H_{2-so} + H_{strain} + H_z \tag{15}$$

where

H_{so} – first order spin-orbit coupling.

H_{2-so} – second order spin-orbit coupling.

H_{strain} – orthorhombic random strain.

H_z – Zeeman interaction.

The Spin orbit coupling terms are given as

$$H_{so} = \gamma\,\lambda\,k_1^{T_1}\,\underline{\ell'}.\underline{S} \tag{16}$$

γ - first order reduction parameter represents the appropriate JT reduction factor.

λ- the spin-orbit coupling parameter and for V^{2+} it has the value of 1500 GHz.

$k_1^{T_1}$ - the isomorphic factor, which most be included when an effective $\ell'=1$ is used. It has the value $(-\frac{3}{2})$ (Bates, 1978).

Equation (16) may be written as

$$H_{so} = a\ \underline{\ell}'.\underline{S} \tag{17}$$

with a = $\gamma\lambda k_1^{T_1}$

$$H_{so} = a\left(\ell'_x S_x + \ell'_y S_y + \ell'_z S_z\right)$$

$$= a\,[\ell'_z S_z + \frac{1}{2}(\ell'_+ S_- + \ell'_- S_+)] \tag{18}$$

Second-order spin-orbit coupling is described by the Hamiltonian :

$$H_{2-so} = \lambda[c\ (E_\theta E_\theta^S + E_\varepsilon E_\varepsilon^S) + b(\underline{\ell}'.\underline{S})^2\,] \tag{19}$$

where

$$E_\theta E_\theta^S + E_\varepsilon E_\varepsilon^S = \frac{1}{4}\left[\{3\ell_z'^2 - \ell'(\ell'+1)\}\{3S_z^2 - S(S+1)\}\right] + \frac{3}{16}\left(\ell_+'^2 + \ell_-'^2\right)\left(S_+^2 + S_-^2\right)$$

and

The parameters b and c depend upon the nature and magnitude of the JT coupling (Al-Sheikh et al., 1998).

The orthorhombic distortion Hamiltonian is given by :

$$H_{strain} = H_{Tet} + H_{Tri} \tag{20}$$

where

H_{Tet} – describe the tetragonal random strain along O_z.

and

H_{Tri} – describe the corresponding trigonal random strain.

$$H_{Tet} = \alpha\,\ell_z'^2 \tag{21}$$

where $\alpha = \frac{2}{3} V_E\,\overline{Q}_\theta$

For strains along O_x , z is replaced by x and α by $V_E\,(-\frac{1}{3}\overline{Q}_\partial + \frac{1}{\sqrt{3}}\overline{Q}_\varepsilon)$. Similarly, for strains along O_y, z is replaced by y and α by $V_E\,(-\frac{1}{3}\overline{Q}_\partial - \frac{1}{\sqrt{3}}\overline{Q}_\varepsilon)$. $\overline{Q}_\partial$ and $\overline{Q}_\varepsilon$ are e-type static strains.

For two of the six orthorhombic sites, H_{Tri} is given as :

$$H_{Tri} = \pm\beta\left(\ell'_x\,\ell'_y + \ell'_y\,\ell'_x\right)$$

$$= \pm\frac{i\beta}{2}\left(\ell_+'^2 - \ell_-'^2\right) \tag{22}$$

Then

$$H_{strain} = \ \alpha\,\ell_z'^2\ \pm\ \beta\left(\ell'_x\,\ell'_y + \ell'_y\,\ell'_x\right) \tag{23}$$

The other four sites are obtained by cyclic interchange of x , y and z.

The effective Hamiltonain is completed by the Zeeman term which is given in equations (12) and (13). Therefore :

$$H_{eff} = a\, \underline{\ell'}.\underline{S} + \lambda b(\underline{\ell'}.\underline{S})^2 + \lambda c(E_\theta E^S_\theta + E_\varepsilon E^S_\varepsilon) + \alpha \ell'^2_z \pm \beta \left(\ell'_x \ell'_y + \ell'_y \ell'_x\right) + g\beta \underline{B}.\underline{S} \qquad (24)$$

DISCUSSION AND CONCLUSIONS

This work presented a theoretical model for GaAs doped with Vanadium, assuming that the TD-EPR results can be attributed to V^{2+} ion with a $^4T_1$ ground state on account of the existence of three closely spaced Kramer's doublets which cross as the magnetic field is increased.

For calculations, it has been modeled H_{eff} as given in eq(15). While a spin Hamiltonian given in eq(14). Values of the constants γ, $g_{||}$, A and the strain parameters D & E can be found by fitting an experimental data. A detailed calculations for H_{spin} and H_{eff} matrix elements, from eq (14) & eq(15), and evaluation of intensities of transitions has started and it is hoped to report on the values of all parameters of this module for GaAs: V^{2+}.

REFERENCES

Al-Sheikh, A.M.; Qiu, Q.C.; Roura, P.; Ulrici, W.; Clerjaud, B.; Bates, C.A. and Dunn, J.L.,1998. Effects of uniaxial stress on the $^2E \rightarrow {}^2T_2$ absorption lines of GaP:T^{3+} and the nature of the Jahn Teller coupling. J. Phys.: Condens. Matter 10, 3367-86.

Atkinson, I., 1987. Acoustic relaxation phenomena in crystalling GaAs doped with transition metal ions. Thesis Univ. of Nottingham, England.

Bates, C. A., 1978. Jahn-Teller Effects in Paramagnetic crystals, Phys. Rep. Phys. Lett. Sect. C, 35C, (3), 187-304.

Bates, C.A. and Stevens, K.W.H.,1986. Localized electron states in semiconductors, Rep. Prog. Phys. 49, 783-823.

Bates, C.A.; Dunn, J.L. and Sigmund, E., 1987. An analysis of $T \otimes (e+t_2)$ Jahn-Teller system with strong coupling, J. Phys. C : Solid State Phys. 20, 1965-83.

Ham, F.S., 1965. Dynamical Jahn-Teller effects in paramagnetic resonance spectra : Orbital reduction factors and partial quenching of spin-orbit interaction, Phys. Rev. A, 138, 1727-40.

Katayama-Yoshida and Zunger, A., 1986. Prediction of a low-spin ground state in the GaAs:V^{2+} impurity system, Phys. Rev. B, 33, 2961-4.

Krebs, J.J. and Staus, G. H., 1977. Confirmation of the EPR identification of Cr^{4+} ($3d^2$) in P-type Cr-doped GaAs by means of applied uniaxial stress, Phys. Rev. B, 15, 17-21.

Kutt, W.; Bimberg, D.; Maier, M.; Krautle, H.; Kohl, F. and Bauser, E., 1984. Heat treatment induced redistribution of Vanadium in semi-insulating GaAs : V, Appl. Phys. Lett. 44, 1078-80.

Rampton, V. W.; Saker, M. K. and Ulrici, W., 1986.Acoustic paramagnetic resonance of Vanadium in semi-insulating GaAs, J. Phys. C: Solid state Phys. 19, 1037-43.

Vasson, A.; En-Naqadi, M. and Vasson, A. M., 1986. Low temperature a caustically detected EPR in alumina and III-V materials, J. Phys. D : Appl. Phys., 19, 1149-57.

Vitton,E.;Fizzotti,F.;Mirri, K.; Gargioni, E.; Polesello, P.; Loguidice, A.; Manfredotti, C.; Galassini, S.; Rossi, P.; Vanni, P. and Nava, F.,1999. IBIC analysis of GaAs shottky diodes.Nuclear Instruments and Methods in Physics and Research B,158, 470-5.