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Jahn-Teller effect in ZnS:Fe^{2+}: a comparison between the method of Glauber states and Born-Oppenheimer states

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The absorption spectra of magnetic impurities in II-VI compounds can only be explained if the Jahn-Tellller effect is taken into account. To cope with this task there is a variaty of methods. In the present work we compare two of them: Born-Oppenheimer method and Glauber states method. The application makes use of the parameters that would be appropriate for the absorption spectrum of ZnS:Fe^{2+}. The only free parameter in our calculations is the Jahn-Teller energy, so we do not attempt here a final description of the spectrum. The emphasis is on the comparison of both methods looking for their validity and divergence conditions and especially the way in which they can reinforce each other to give a more reliable description of these spectra.

Keywords: Absorption spectra; Jahn-Tellller effect; Jahn-Teller energy; Born-Oppenheimer states; Glauber states

Los espectros de absorción de impurezas magnéticas en compuestos II-VI sólo pueden ser explicados si se considera el efecto Jahn-Teller. Para realizar esta tarea existen variados métodos. En este trabajo se comparan dos de ellos: el de Born-Oppenheimer y el de estados de Glauber. La aplicación hace uso de los parámetros apropiados al espectro de absorción del ZnS:Fe^{2+}. El único parámetro ajustable en nuestros cálculos es la energía de Jahn-Teller, por lo que no intentamos aquí una descripción final del espectro. El énfasis está en la comparación de los métodos, sus condiciones de validez o divergencia y, muy especialmente, la forma como se pueden reforzar para dar una descripción más confiable de los espectros de estos sistemas.

Descriptores: Espectros de absorsion; efecto Jahn-Tellller; energía Jahn-Teller; estados de Born-Oppenheimer; estados de Glauber

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1. Introduction and theory

The absorption spectra of magnetic impurities in II-VI compounds shows more zero-phonon lines than expected from plain crystal-field theory even when spin-orbit interaction is included to very high order of accuracy [1–3]. This phenomenon is rather weak for ZnS:Fe^{2+} and is very important for CdTe:Fe^{2+}, with intermediate situations for other II-VI compounds [4]. Several authors have proposed that this is the manifestation of a Jahn-Teller (JT) effect [3–5].

In the present paper we would like to compare two methods applying them to the case of ZnS:Fe^{2+}, in which the JT effect appears as the weakest of the series of Fe in II-VI compounds. The absorption spectrum shows a strong line at 2945 cm^{-1}, followed by very weak lines at intervals of 19 cm^{-1} and 39 cm^{-1} respectively. For higher energies a more complex structure is present where phonon-assisted transitions begin to dominate. No attempt will be done at this moment to explain every line and intensity, but the leading three lines (two energy intervals) will be taken into account below.

The crystalline field at the position of the impurity has a symmetry T_d which splits the ^5D atomic multiplet into ^5E and $^5T_2$ multiplets. Spin-orbit interaction further splits these levels: the ground ^5E multiplet forks in 5 levels leaving a singlet (A_1 or γ_1) as the true ground state from which absorptions will originate at low temperatures. The excited $^5T_2$ multiplet splits into 6 levels, two of which are of symmetry T_2 or Γ_5 which are candidates for final states in electric-dipole transitions. However, these two states would be separated by energies of a few hundreds cm^{-1} so they cannot explain three low-energy lines spread in less than 100 cm^{-1}. A complete energy-level diagram supporting this discussion can be found in Ref. 4.

Next step is to decide on the coupling phonons. Here we will assume that such vibrational mode must have an important local component in the surrounding tetrahedron of 4 anions. The simplest possible local mode would be a doubly degenerate ε modes, Q_θ and Q_ϵ, to which usual creation and annihilation operators apply.

The total Hamiltonian comprises the electronic component, the vibrational component of the coupling modes and the Jahn-Teller or coupling component. The latter can then be written as

$$H_{JT} = \sqrt{E_{JT}\,\hbar\omega}[(a_\theta^\dagger + a_\theta)D_\theta + (a_\epsilon^\dagger + a_\epsilon)D_\epsilon]\,, \qquad (1)$$

where E_{JT} is the Jahn-Teller energy or strength of the coupling, $\hbar\omega$ is the energy of the coupling mode, D_θ and D_ϵ are normalized operators acting on the electronic orbitals.

To diagonalize the total Hamiltonian a complete basis of vibronic functions is needed. Such basis can be constructed in several ways. Here we will do so using bases constructed in two extreme cases.

On one hand, we will construct the basis in the weak coupling limit, by taking direct products of vibrational functions and electronic funtions. This is the so-called adiabatic or Born-Oppenheimer limit. Vibrational functions are progressively built increasing

$$N = n_\theta + n_\epsilon, \tag{2}$$

the number of vibrational quanta, where n_θ and n_ϵ are the ocupation numbers of normal modes Q_θ and Q_ϵ respectively. The details about the construction of this basis have been given elsewhere [4].

On the other hand, we consider that the coupling could be so large as to initially produce a virtual distortion. Equilibrium is now reached by a mixture of electronic and vibrational coordinates. The system is then allowed to vibrate in the distorted positions. Such displaced harmonic oscillators can be described by means of Glauber states increasing the total vibrational quantum number N in a progressive way in the same manner introduced above. This method has also been reported previously in the literature [6–10].

We have developed algorithms to diagonalize the total Hamiltonian in both bases defined in previous paragraphs. In the rest of this paper we will go directly to the comparison of numerical results obtained by using the same parameters in both calculations.

2. Results and discussion

The crystal-field parameter $10|Dq|$ for ZnS:Fe^{2+} has been estimated to be 3158 cm^{-1} based on general considerations of the threshold absorption line [5]. We use here the free ion value of the spin-orbit parameter. Namely, $\lambda = -100$ cm^{-1}. The coupling mode has been taken as the TA2(K) mode of ZnS, which is very abundant in the lattice dynamics [11], and has the appropriate projection of ε modes in the local symmetry surrounding the Fe impurity ion. That is to say $\hbar\omega \approx 85$ cm^{-1}, which will be considered as 100 cm^{-1} in this general presentation to facilitate comparison of magnitudes. Then the only parameter that can be varied is the coupling constant or, rather, the Jahn-Teller energy, E_{JT}.

Results will be presented in figures that have the following common considerations: (a) We consider the six lowest energy levels by showing the 5 energy differences referred to the lowest level. (Notice that the lowest energy difference is 0 coinciding with the axis). (b) Results for Born-Oppenheimer method will be represented by discontinuous lines; (c) Results for Glauber method will be represented by continuous lines.

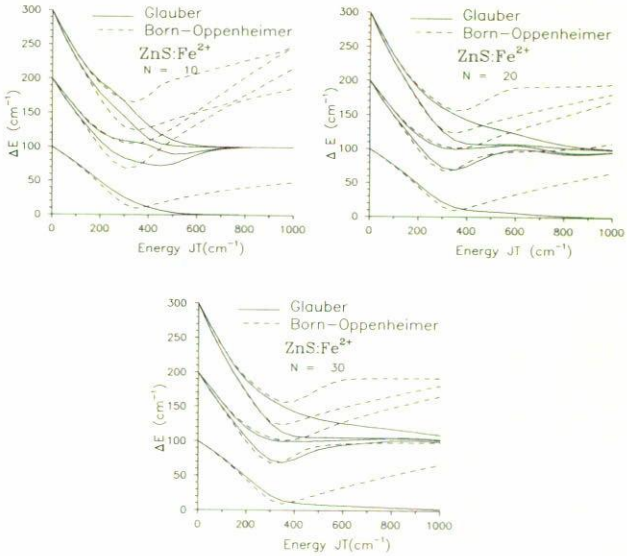

FIGURE 1. Six lowest vibronic energy levels (five energy intervals) as functions of the Jahn-Teller energy using the following parameters for both methods: $10|Dq| = 3158$ cm^{-1}, $\lambda = -100$ cm^{-1}, $\hbar\omega = 100$ cm^{-1}. Three different values for $N = n_\theta + n_\epsilon$ are illustrated: 10, 20 and 30.

In Fig. 1 we report the 6 energy levels as functions of E_{JT} for three different values of N: (a) for $N = 10$; (b) for $N = 20$; (c) for $N = 30$.

Several comments follow from Fig. 1. First, we realize that both methods converge to the appropriate $0\,\hbar\omega$, $1\,\hbar\omega$, $2\,\hbar\omega$, etc. values in the case of entirely decoupled modes. Second, in the low-coupling limit ($E_{JT} < |\lambda|$ and $E_{JT} < \hbar\omega$) both methods give similar results and the small differences tend to disappear as N increases. Third, in the strong-coupling limit ($E_{JT} \gg |\lambda|$ and $E_{JT} \gg \hbar\omega$) only the Glauber method converges to the appropriate $0\hbar\omega$, $1\hbar\omega$, etc. values; Born-Oppenheimer states tend to diverge even when N is substantially increased.

The intermediate case ($E_{JT} \approx |\lambda| + \hbar\omega$, roughly speaking) deserves a more extense discussion. The Born-Oppenheimer results go through a minimum over which levels tend to diverge rather quickly. Such behavior is unphysical, representing the limitations of the method which is intended for weak coupling. Then, this method can be trusted only in the regime in which the levels loose energy, closing the energy intervals. For the example under consideration, $E_{JT} \approx 300$ cm^{-1} is an upper limit for this application. On the other hand, the results of the Glauber method present oscillations in the region of intermediate coupling. However, these fluctuations move to higher values of E_{JT} and tend to disappear as N grows. To have reliable results with the Glauber method, it is enough to study the stability of the solutions with respect to N. Eventually we can always get to a value of N for which stable results are found.

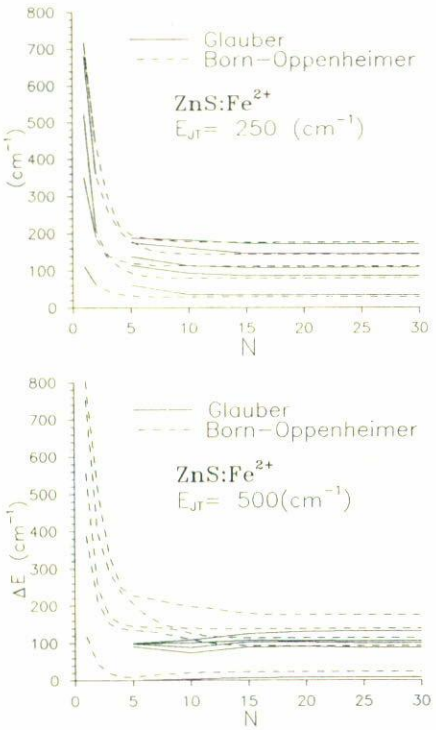

FIGURE 2. Six lowest vibronic energy levels as functions of $N = n_\theta + n_\epsilon$. Parameters are the same used for Fig. 1. Two different values for E_{JT} are illustrated: 250 and 500 cm^{-1}.

In Fig. 2 we study stability of the 5 lowest energy intervals for 2 values of the Jahn-Teller energy: (a) 250 cm^{-1}, and (b) 500 cm^{-1}.

In Fig. 2a we realize that the Born-Oppenheimer method is already stable at $N = 10$, while Glauber states need up to $N = 15$ to stabilize the 6 low laying vibronic levels. We also notice that the results given by both methods for the 6 energy levels are very similar.

Figure 2b presents a clear disagreement of the two methods. Although they are stabilized for $N = 20$ at least, they give completely different numerical results. It is expected that for this coupling energy, the two lowest levels should tend to degenerate at $0\hbar\omega$ while the other four levels should also degenerate at abouth $1\hbar\omega$ over the ground doublet [9]. This is shown by the Glauber results but not by the Born-Oppenheimer calculations.

3. Concluding remarks

We conclude by saying that the Born-Oppenheimer method can be applied only for weak coupling, *i.e.* for $E_{JT} \leq |\lambda| + \hbar\omega$. The case under study seems to be at the limit of applicability of this method. Fortunately the method of Glauber states, for $N > 15$ is stable enough to allow a more realistic calculation trying to optimize the found intervals to explain the spectrum.

Both methods explain the decrease in the enrgy intervals in order to explain experimental spectra. Figure 2a can be used at this time as a preliminary explanation of this general

phenomenon. We realize that both methods give the first two intervals under the assumed energy for the coupling phonon 100 cm^{-1}, which is very encouraging. The calculated values are about 30 and 80 cm^{-1} for the parameters reported in this figure, which are still larger than the observed small peaks at 19 and 39 cm^{-1}. However, from Fig. 1c we can see that a better adjustment can be obtained by considering a lower (more realistic) phonon energy and tuning the Jahn-Teller energy in a more careful way. This goal is out of the scope of the present work since it would require the distillation of the wave functions to calculate the corresponding the electric dipole intensities to look for a complete correspondence with the spectrum.

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