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Temperature dependence of impurity levels in bulk semiconductors

(Estudo do efeito térmico sobre os níveis de impurezas em semicondutores)

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The temperature dependence of impurity levels in semiconductors is a very interesting problem in the domain of deep levels impurities. Its evidence in experimental results is reported by many authors. However, the interpretation on theoretical basis requires sophisticated models. In this paper we propose a very simple model that allows to extract the relevant parameters from the experiment without needing heavy computation.

Keywords: bulk semiconductors, impurity levels, thermal properties.

O estudo da dependência da posição dos níveis de energia das impurezas profundas em semicondutores com a temperatura é um problema bastante interessante, e sua evidência experimental é discutida por vários autores. Neste artigo propomos um modelo teórico bastante simples, a partir do conhecimento da secção de choque de fotoionização e de alguns parametros associados aos fónons, para o entendimento deste comportamento.

Palavras-chave: semicondutores volumétricos, impurezas profundas, propriedades térmicas.

In recent years progress has been made in investigating the physical properties of impurity centres in semiconductors either theoretically or experimentally. For deep level impurities their identification and characterisation remains as a difficult problem and it is still an important and active field in semiconductor research [1]. On the other hand, many of the shallow impurities are by now well understood. The effective mass theory of shallow impurities [2] led to the well-known hydrogenic theory providing both conceptual guidance and, in many cases, quantitative predictions about the binding energies [3]

However, one major difficult to obtain accurate solutions to the problem is the presence of the interaction between the electrons and the lattice. The model generally used for a quantitative treatment of electron-phonon interaction is the so-called configuration coordinate model. Its formalism has developed a long time ago and reviews exist on this topic for semiclassical as well as quantum treatment [4, 5, 6]. In its original form this model is worked out for transitions within localised states, and it has been applied successfully to such systems as F-centres in alkali halides and rare-earth impurities in semiconductors. It is also widely accepted for studying transitions related to deep centres, mainly due to a large Franck-Condon shift [7].

It is generally accepted that even were a full theory available, it would be necessary to extract from it an acceptable, simplified model which could be used to define the principal measurable quantities and to provide a useful terminology for describing experimental results. The presence of such a model is of some importance and we attempt in this article to illustrate what experimental features lend themselves most readily to modelling.

Whilst many of these subjects can readily be discussed in a qualitative way in an undergraduate class, it is difficult to go into the theory underlying the thermal process unless the students have a sound background in solid state theory. However, some important quantitative features of the process can be conveyed by elementary methods described in this paper.

The temperature dependence of the energy levels in semiconductors is discussed in Ref. [8] for different types of defects in Si and Ge, and in Refs. [9] and [10] for some deep levels in compound semiconductors. In particular Ref. [11] provides a detailed discussion of thermodinamics functions involved in the thermal processes associated impurities in semiconductors. A rather common technique applied to interpret the experimental results is the convolution method. An exaustive discussion of this method can be find in Ref. [12] and references therein.

In order to proceed for the study of the temperature dependence of the energy levels, we just make an attempt to look and understand these effects in terms of

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thermal broadening. We also admit that the primary effect of the electron-phonon coupling is to shift the edge of the photoionisation cross section [13]. Thus, we may write

$$E_I \rightarrow E_I^o + S\hbar\omega_p \tag{1}$$

where E_I is the ionisation energy, S a measure of the electron-phonon coupling (the Huang-Rhys factor), $\hbar\omega_p$ the phonon energy that takes part in the electronic transition, which we admit a transition from a donor-like impurity to the conduction band, and E_I^o is the the optical ionisation energy in the absence of electron-phonon coupling ($S = 0$). More realistically, the coupling with the lattice introduces a temperature dependence of photoionization cross section and a shift in the threshold energy. An interesting discussion involving indirect transitions is given in Ref. [14].

To model this effect most simply we will assume that the lattice coupling does not strongly affects the shape of the spectral dependence, but merely shift the threshold energy by an amount proportional to the temperature [15]

$$E_I(T) = E_I(0) - \beta_T T, \tag{2}$$

where β_T is the temperature coefficient of the apparent shift of energy with temperature caused by thermal broadening, and $E_I(0)$ is the threshold energy

$$E_I(0) = E_I^o + S\hbar\omega_p. \tag{3}$$

Essentially, what we have done is to associate thermal broadening with the apparent shift of threshold energy with temperature. Its origin is in the temperature dependence of emitted phonons, p, which maximizes the transition rate W_p [13]

$$W_p \approx |M|^2 \, J(E_p)\rho(E_{\mathbf{k}}) \tag{4}$$

where $|M|^2$ is the electronic matrix element, and $\rho(E_{\mathbf{k}})$ is the electronic density of states, $J(E_p)$ is the square of the matrix element involving the overlap of displaced oscillator wavefunctions [16] for the case of emitting an energy E_p in phonons. It also accomodates the case of absorption, in this case, E_p being negative. $J(E_p)$ maximizes at all temperatures when $p = S$. We illustrate this behaviour in Fig. 1, for $S = 3.0$ and an effective temperature $T^* = 1.0$ in units of $\hbar\omega_p/k_B$.

However, due to the dependence of W_p and $\rho(E_{\mathbf{k}})$ on the final states with energy $E_{\mathbf{k}}$ the maximum of W_p is not at $p = S$ but at a value of p less than S, since for phonon emission process the transition rate increases with $E_{\mathbf{k}}$, and $E_{\mathbf{k}} = h\nu - E_I - p\hbar\omega_p$, with $h\nu$ being the energy of the incident radiation [17]. Moreover, this value of p decreases with increasing temperature as the dependence of $J(E_p)$ on p become less pronounced, and it is this temperature-dependence which causes the apparent threshold to vary.

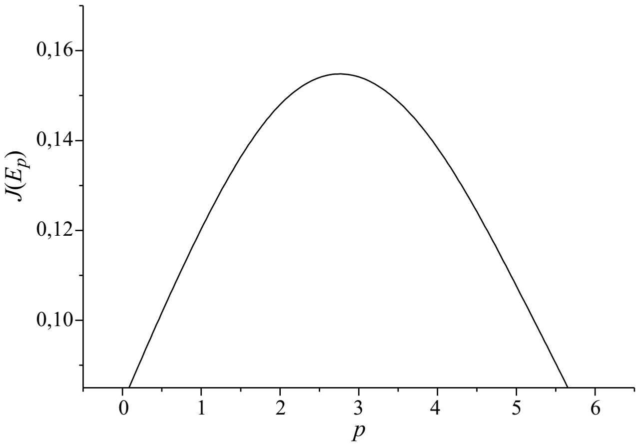

Figura 1 - Behaviour of $J\,(E_p)$, for $S = 3.0$ and an effective temperature $T^* = 1.0$ in units of $\hbar\omega_p/k_B$.

As an illustration, this behaviour of the photoionisation cross section [18] for a donor type impurity with photon energy at different temperatures is shown in Fig. 2, for a trap state with ionisation energy $E_I^o = 20\hbar\omega_p$ [19].

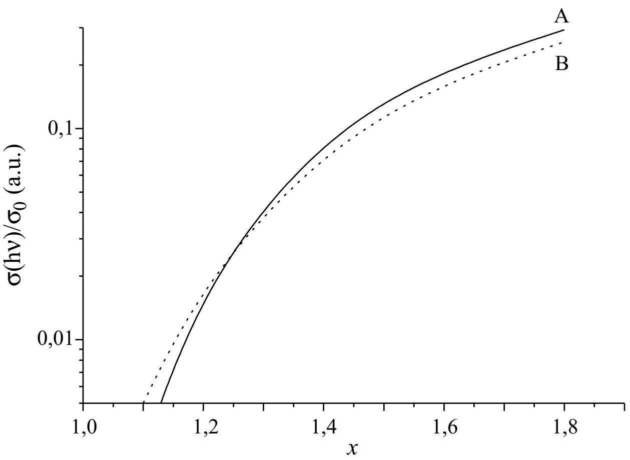

Figura 2 - Photoionization cross section for neutral donor centre ($\sigma(h\nu)$), with $x = \frac{h\nu}{E_I}, E_I^o = 20\hbar\omega_p$. The curves are for phonon-coupling strength $S = 3.0$ for temperatures A, $T^* = 1.0$, B, $T^* = 0.1$, in units of $\hbar\omega_p/k_B$.

Although Eq. (2) is an empirical equation, we have to provide a way to obtain β_T. This temperature coefficient is derived graphically from plots similar to those shown in Fig. 4 for various values of S, $\hbar\omega_p$ and E_I^o. The procedure for obtaining this coefficient is depicted in the following paragraphs.

A plot of $[\sigma(h\nu) \cdot h\nu]^{2/3}$ *vs.* $h\nu$ for three different values of temperature in units of $\hbar\omega_p/k_B$ is depicted in Fig. 3. It shows an apparent change in the threshold of the ionisation energy, and as we get near this threshold the curve bends upwards due tho the presence of phonons in the transition. A linear fitting of this curve provides the threshold ionisation energy due to photon absorption, or the optical ionisation energy as a function of temperature $E_I(T)$. So, for different temperatures one gets different values of $E_I(T)$. However, the photoionisation cross section is sensitive to different values of S, and so should be this threshold energy. This behaviour is shown in Fig. 4.

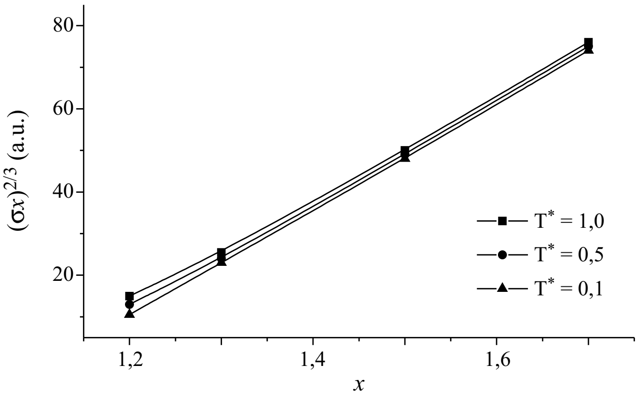

Figura 3 - $(\sigma(h\nu))^{3/2}$ *vs.* $h\nu$ (Lucovsky Plot) for three different temperatures $T^* = 1.0$, $T^* = 0.5$, and $T^* = 0.1$ as indicated in the insert.

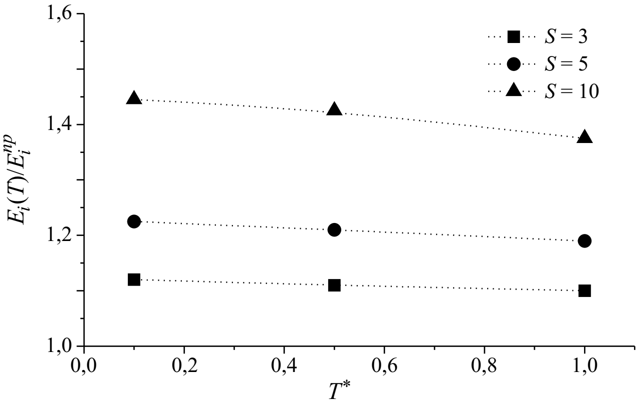

Figura 4 - Temperature dependence of the optical ionization energy, for three different values of the phonon coupling $S = 3.0$, $S = 5.0$, and $S = 10.0$, as indicated in the insert.

A linear fit of these curves provides β_T and $E_I(0)$

$$E_I(T) = E_I(0) - \beta_T T. \tag{5}$$

Yet the coefficient β_T in the above equation depends on E_I^o, S and $\hbar\omega_p$. For electrons making a transition between $|s\rangle$-like states only the zone edge LA and LO phonon energies are involved [20], so $\hbar\omega_p$ is in principle known. However, neither S or E_I^o is obtained separately from this observation of effective threshold. To circumvent this problem one has to obtain a relation between (β_T) and $\frac{S\hbar\omega_p}{E_I^o}$. Figure 5 provides a way to obtain such relation. From the graph we obtain:

$$\beta_T \approx \beta_0 \frac{S\hbar\omega_p}{E_I^o},$$

with $\beta_0 \simeq 3.2k_B$, where k_B is the Boltzmann constant and β_T is proportional to S. As expected, inserting this into Eq. (5) one recovers Eq. (3).

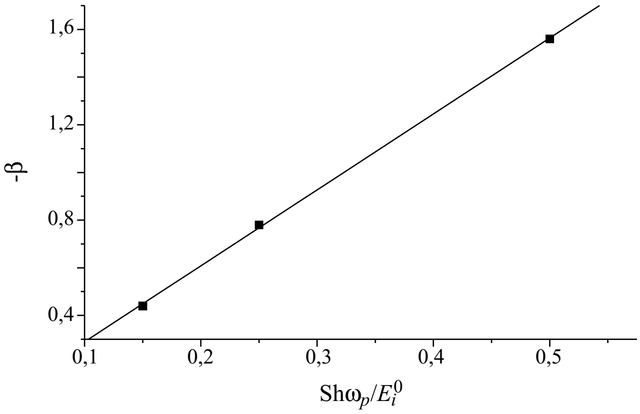

Figura 5 - Temperature coeficient of the apparent shift of energy with temperature (β_T) as a function of $\frac{S\hbar\omega_p}{E_I^o}$.

Measured values of cross sections, or more usually, of a quantity proportional to $\sigma(h\nu)$ such as photosensitivity - the change in photoconductivity per photon, which are used to obtain the effective threshold in the way described in this paper, span typically an order of magnitude near the shoulder of the spectral-dependence curve. Below this region lies a spectral tail which extends through and below the effective threshold, spanning two or more orders of magnitude. The form of this tail is sensitive to temperature and to lattice-coupling strength, and provided it is not influenced by lower energy optical transitions, its form and temperature dependence can be analysed to provide a measure of S. One may wonders about the effect of the band-gap energy as it also depends on temperature on the determination of $E(T)$. Rather than going into the calculations in order to obtain the relevant thermodynamics parameter, such as the Gibbs free energy and thus the entropy, we suggest that it may additive, so we should include into Eq. (2) a term similar to one encountered in Varshini equation [21].

In this paper one tries to provide a simple method which could be easily applied to experimental results in order to extract relevant parameters and replace heavy computation, along the same lines we have proposed in Ref. [22]. In an experiment one does not know the charge of the centre, and one does not need to know the charge to obtain something useful, so its effect is not include in this simple model. Also, the size of the centre is not included. As a step forward one proposes an empirical formula for temperature dependence of the energy threshold associated with optical transitions involving impurities in semiconductors. In summary, the model described in this paper is undoubtedly over-simplistic, and should not be regarded as anything more than a conceptual aid. On the other side, it does provide an easily understood introduction to the subject, and may enable some useful quantitative results to be obtained without a detailed quantum mechanical calculations.

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