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THE ABSENCE OF EXCHANGE OR MOTIONAL NARROWING OF E.S.R. ABSORPTION LINES, THE SPATIAL EXTEND OF THE LOCALISED PARAMAGNETIC CENTRES AND THE ROLE PLAYED BY THE CHARGE-LATTICE INTERACTION IN AMORPHOUS SEMICONDUCTORS WITHOUT AND WITH HYDROGEN

Petr VIŠČOR

Faculté des Sciences, Université de l'Etat, Avenue Maistriau, 23
7000 - Mons (Belgium).

The absence of any sizable exchange or motional narrowing of the electron spin resonance absorption lines for samples with high concentration of homogeneously distributed spins indicate that the paramagnetic centres in amorphous Ge and Si are severly localised. An upper limit to the decay parameter α of the spatial extend of the wavefunction describing the "free" spin in shown to be less than $\alpha^{-1} < 2.5$ Å. If different charge states of the paramagnetic centres are assumed to exist within the gap of amorphous Si and Ge, large charge-lattice interaction is therefore required in order to offset the Coulomb repulsion. A possible model for the electron states in the gap of hydrogenated amorphous silicon (doped or undoped) is proposed which takes this into account explicitly.

Spatial extend of localised wavefunctions in a-Si from E.S.R. and magnetic susceptibility studies. The absorption line g = 2.0055, usually named as "dangling bond" line is a remarkably common feature, occurring in all forms of a-Si. The maximum value (the upper bound) for the α^{-1} for this line can be estimated from the upper bound on the strength of the exchange interaction which in turn can be estimated from possible deviations of the magnetic susceptibility from the normal Curie behaviour at low temperatures. Taking the results on ultra high vacuum (UHV) evaporated a-Si[1] with $N_s \cong 10^{20}$ cm^{-3} (homogeneous distribution) and with the upper bound on the exchange interaction to be fraction of a degree (Curie behaviour observed down to the lowest temperatures measured), one arrives at a value of $\alpha^{-1} \leq 2.4$ Å (a-Si) and $\alpha^{-1} \leq 3.0$ Å for a-Ge. The absorption lines g = 2.011 and g = 2.0043 which are also seen in the E.S.R. signal of amorphous hydorgenated silicon (a-Si:H) have been assigned[2,3] to the valence "band tail" holes ($\alpha^{-1} \cong 8$ Å) and the conduction "band tail" electrons ($\alpha^{-1} \cong 150$ Å). The lines are observed in boron doped (g = 2.011), phosphorous doped (g = 2.0043) but also in the undoped material when illuminated with band gap light (in this case both lines are observed). The quoted values of α^{-1} for the two cases are quite unreasonable in view of the absence

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of exchange narrowing in the first case and of motional narrowing in the second. It is therefore evident that while the upper bound for α^{-1} of the "dangling bond" paramagnetic centre is 2.4 Å, no unambiguous estimates can be made at present concerning the two "band tail" lines.

Doubly occupied "dangling bond", Coulomb repulsion and the magnitude of the charge-lattice interaction. The Coulomb repulsion between the two electrons residing on the same "dangling bond" centre should be expected to lie somewhere between the unscreened value of $U < e^2.\alpha \tilde{=} 6.0$ eV (if the second electron's wavefunction is characterised by the same α^{-1}) and the fully screened value of $U > e^2.\alpha/\varepsilon(0) \tilde{=} 0.625$ eV (here e is the elemental electrical charge and $\varepsilon(0)$ is the static dielectric response function of the material) Because of the Coulomb repulsion between the two electrons residing on the same "dangling bond" being of the order of the gap energy or more it is clear that for this level to lie somewhere within the gap when doubly occupied (as required by the experimental evidence from the doping studies), there must be quite an appreciable lattice distortion around the centre (again of the order of the gap energy) in order to offset the Coulomb repulsion and push the doubly occupied energy level back into the gap.

The most direct experimental demonstration of the relatively large magnitude of the charge-lattice interaction comes from the very important total yield photoemission spectroscopy experiment on undoped and P-doped hydrogenated amorphous silicon by Griep and Ley[4] (identification of a band of localised electron states some 0.45 eV above the top of the valence band).

At first glance the result of this experiment seems to present quite a dilemma since the photoemission total yield signal from the band in the gap increases with increasing N_s of the "dangling bond" centres in the first case while it increases with the decreasing N_s in the second! This contradiction is however resolved if the singly and doubly occupied "dangling bond" centres in a-Si:H both lie at approximately same energy of 0.4 - 0.5 eV above the valence band edge!

Localised charges with finite charge-lattice interaction and the Thomas-Fermi statistics. The acceptance of the importance (at least in principle!) of the charge-lattice interaction when investigating the nature and the dynamics of the localised states in the gap of a-Si and a-Ge has an important consequence in so far as the

appropriate statistics of these charges is concerned. The localised electron with an appreciable lattice distortion around it will cease to exhibit pure Fermion-like properties and can not be therefore described adequately by Thomas-Fermi statistics. At high enough temperatures the simple, classical Boltzmann statistics will however be adequate.

Model for the gap states in hydrogenated amorphous silicon (undoped or doped). Following the spirit of the arguments just put forward it should be now possible to sketch out a qualitative, schematic model of the gap states in a-Si:H (whether doped or undoped) which would be hopefully consistent with most of the experimental evidence concerning the gap states in this material[5].

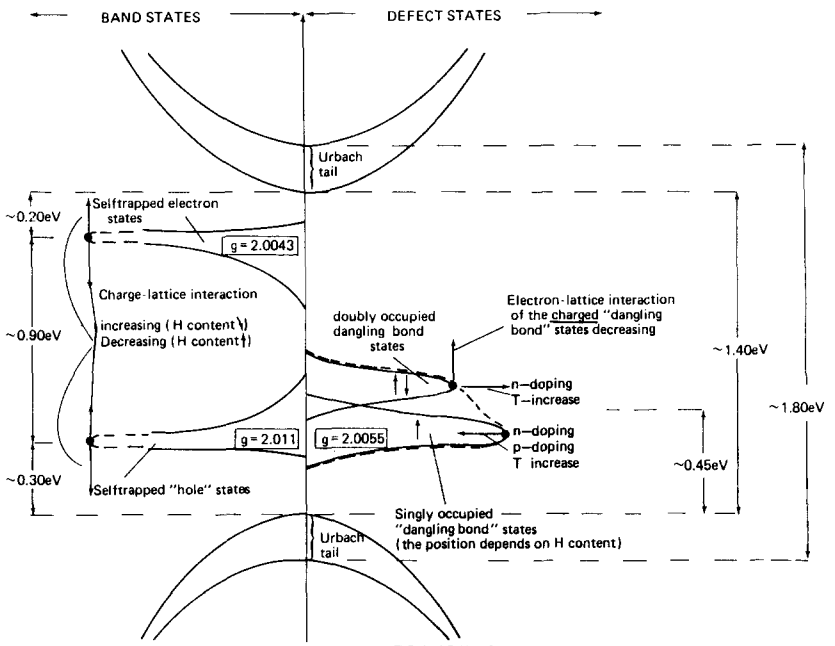

FIGURE 1
A model for the localised electron gap states in a-Si:H

A possible model along these lines in shown in Fig. 1. Here the two E.S.R. lines with g = 2.0043 (band tail electrons) and g = 2.011 (band tail holes) are assigned to selftrapped electrons and holes respectively. It has to be stressed that both these bands are dynamical in the sense that they exist in the gap only when occupied by a charge (the optical transitions into these bands to not exist). Also shown in Fig. 1 are the two charged states of the "dangling

bond" paramagnetic centre (g = 2.0055) forming a band in the gap some 0.45 eV above the valence band edge as observed by the total yield photoemission spectroscopy[4].

The role of hydrogen in Si and Ge amorphous networks. It is usually assumed that the main role of hydrogen in a-Si and a-Ge is to decrease the density of the "dangling bond" centres, thereby increasing the lifetime of the carriers excited into the extended states. However, the recent measurements of the transient photoconductivity[6] in unhydrogenated a-Ge showed that the lifetime of the carriers in the extended states was some three orders of magnitude lower than that of the carriers in the hydrogenated sample with approximately the same density of "dangling bond" defects! It seems therefore quite likely that the main role of hydrogen in amorphous networks of Ge and Si is in fact to stiffen the networks, thereby lowering the charge-lattice interaction (the effect is indicated by arrows in Fig. 1). The consequence of this decrease is the reduced probability for seftrapping which in turn increases the carrier lifetime in the extended states making these making these materials technologically usable.

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