The 2.7 eV photoluminescence band in high-purity synthetic silica

1994 J. Phys.: Condens. Matter 6 6345

(http://iopscience.iop.org/0953-8984/6/31/033)

J. Phys.: Condens. Matter 6 (1994) 6345–6352. Printed in the UK

The 2.7 eV photoluminescence band in high-purity synthetic silica

M Bertino†, A Corazza, M Martini‡, A Mervic and G Spinolo
Dipartimento di Fisica, Università degli Studi di Milano, Via Celoria 16, 20133 Milano, Italy

Received 30 March 1994

Abstract. The 2.7 eV photoluminescence emission ('gamma' band) has been studied in neutron-irradiated high-purity synthetic silica, both under UV and VUV (vacuum ultraviolet) excitation. Some aspects of the 5 eV excitation band, which is already known to exist, have been studied in great detail, while an excitation band centred at about 7.7 eV has been analysed for the first time. The intensity of the gamma emission for 5 eV excitation changes as a function of temperature in a completely different way to that for 7.7 eV excitation. In the latter case the emission intensity is constant up to about 300 K; a non-radiative decay predominates at higher temperatures. For excitation at 5 eV, the 'anomalous' increase of the emission that is already known to occur is observed as the temperature rises up to 500 K. We have developed a phenomenological model relating to the electronic levels of the luminescence centre that fits the experimental data well.

1. Introduction

A number of emission bands have been known of for many years in SiO_2, both in the crystalline and in the amorphous form, but, so far, few definite structural models of the defects responsible have been generally accepted.

The presence of an emission at 2.7 eV in the photoluminescence spectra of silica has been known of since the work of Garino Canina [1], where evidence for three main bands at about 4.3, 3.1 and 2.7 eV, named alpha, beta and gamma, respectively, was found. Recent photoluminescence studies of unirradiated silica [2, 3] related in a convincing manner the emission at 2.7 eV to oxygen deficiency. The same emission, also detected in phosphorescence [4] and in cathodoluminescence spectra [5], is found in all types of neutron-irradiated samples [2, 6].

We could summarize as follows its optical behaviour: it is excited at about 5.0 eV, the region where most of the silica emissions are excited, and also by 7.9 eV excimer laser, both in unirradiated [7] and in neutron-irradiated samples [6], but its excitation spectrum in the vacuum ultraviolet region has never been studied. The temperature dependence of the emission intensity, under 5 eV excitation, exhibits an anomalous behaviour, increasing as the temperature is raised up to 500 K [1, 2]. It appears to be different in neutron-irradiated, excimer-laser-excited samples [8]. The emission lifetime has been measured both in unirradiated and in neutron-irradiated specimens under 7.9 eV laser [8] and 5 eV light [2] and turned out to be 10 ms, independent of the temperature up to 300 K.

Two models have been proposed for the defect responsible for the 2.7 eV emission, both related to oxygen deficiency: the neutral oxygen vacancy [3], i.e. the bond between

† Present address: Max-Planck-Institut für Strömungsforschung, Bunsenstrasse 10, D-3400 Göttingen, Germany.
‡ Author to whom any correspondence should be addressed.

0953-8984/94/316345+08$19.50

two silicon atoms and the twofold-coordinated silicon [2], i.e. a silicon atom linked to two, instead of the usual four, oxygen atoms.

In order to describe better the electronic energy level scheme of the centre involved, we have carried out a detailed study on the 2.7 eV emission band for neutron-irradiated synthetic silica samples. We made this choice because from all the studies that we have performed up to now, we concluded that this emission is due to an intrinsic defect and is independent of the type of silica, (irradiated or not); we chose the situation with minimum interference with other emissions.

We measured emission and excitation spectra both at 5 eV and at 7.6 eV in the temperature range 80–580 K. The temperature dependence of the peak position together with the dependence on the exciting energy has also been studied. Completely different behaviours as functions of temperature, were found when exciting in the two energy regions: using 7.6 eV photons the emission intensity is constant up to 300 K, where a non-radiative recombination path is activated; exciting at 5 eV the already known 'anomalous' behaviour is found. To account for this behaviour, we propose a phenomenological model that fits the experimental data well.

2. Experimental procedure

The measurements we report have been performed mainly on neutron-irradiated dry (OH content < 10 ppm) synthetic silica, Tetrasil SE. As a comparison, measurements on wet (OH content $\simeq 1000$ ppm) synthetic silica, Tetrasil B, were also carried out.

Neutron irradiations were performed at the nuclear reactor of ENEA (Casaccia, Italy). Neutrons with energy in excess of 22.6 eV constituted $\sim 30\%$ of the total flux. During irradiation, the sample temperature was $65 \pm 2\,^{\circ}C$. Total integrated neutron fluxes ranged from 3×10^{15} to 3×10^{18} neutrons cm^{-2}. All samples were disks (diameter 10 mm and thickness 1 mm) with optical-grade polished surfaces.

Photoluminescence excitation in the 4.5 eV–8.5 eV range was produced by a Hinteregger hydrogen discharge lamp (Model 630, McPherson), followed by a grating monochromator (Model 218, McPherson) operating in a hydrogen atmosphere. The spectral band-pass of the excitation was 2.65 nm, corresponding to 104 meV at 7 eV. The photoluminescence in the 2.5 eV–5.0 eV spectral range was analysed with a grating monochromator (Model 82-410, Jarrel–Ash) followed by an EMI 9924QA photomultiplier (Bialkali photocathode). The spectral band-pass with 13.2 nm, corresponding to 96 meV at 3.0 eV.

Measurements in the 80 K–370 K temperature range were performed on samples kept in high vacuum ($\sim 10^{-6}$ Torr). All PL spectra were corrected for the spectral response of the optical system. The PLE spectra were corrected for the spectral distribution of the excitation intensity.

3. Results

Since the first luminescence studies, it has appeared that the gamma emission is excited at around 5 eV; more recently, it was found that the same emission could be excited in the vacuum ultraviolet (VUV) region as well [6, 7], both in unirradiated and in neutron-irradiated samples under excimer laser excitation, but no excitation spectra have been presented so far.

Let us first describe our excitation studies at around 5 eV. In a recent paper [9] we mentioned preliminary results according to which upon exciting both unirradiated and

neutron irradiated silica samples in the 5 eV region, the emission peak energy shifted (increasing the emission energy) as the excitation energy was increased. We here confirm that result—see figure 1, in which the gamma band of a neutron-irradiated dry synthetic silica sample (Tetrasil SE) at a temperature of 573 K is shown, for two different excitation energies (4.60 and 5.16 eV). We report high-temperature measurements, because the intensity of the gamma band is lower at low temperatures, as mentioned in the introduction and as will be discussed in the following.

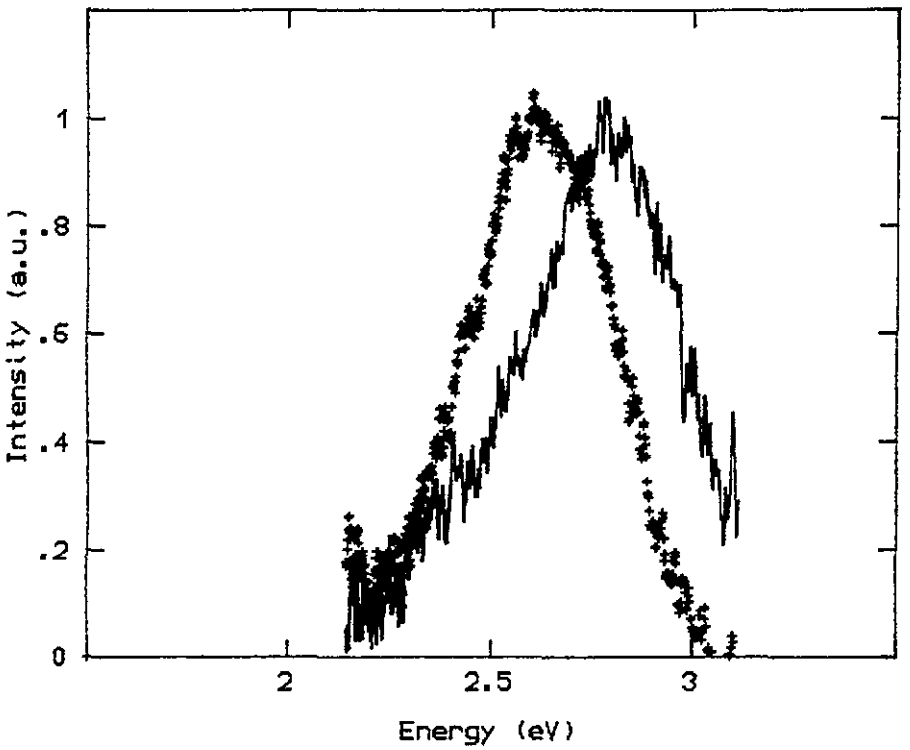

Figure 1. Photoluminescence spectra of the 2.7 eV emission band measured at $T = 573$ K of a Tetrasil SE (type IV) sample irradiated with 3×10^{18} neutrons cm^{-2} excited by two different excitation energies: crosses, 4.60 eV; lines, 5.16 eV. The spectra are normalized at the maximum.

The shift of the energy of the emission band is summarized in figure 2, in which it can be seen that there is a dependence on the temperature as well: the emission energy increases as the temperature is raised. This behaviour is quite unusual: most of the emission bands exhibit a red shift in place of the present blue shift, increasing the temperature.

We have also excited the gamma band in the VUV region and, contrary to what we detected for excitation at around 5 eV at $T > 300$ K, the gamma emission energy does not vary following the excitation energy; its value is invariably 2.77 ± 0.04 eV in the temperature range from 100 to 370 K. At higher temperatures the emission is quenched by competing non-radiative processes. The excitation band peaks at 7.7 eV, as shown in figure 3.

We also studied the temperature dependences of the intensity of the gamma band, exciting both at 5 eV and at 7.7 eV. They are markedly different as can be seen in figure 4: in the temperature interval 80–250 K the gamma intensity is constant for excitation at

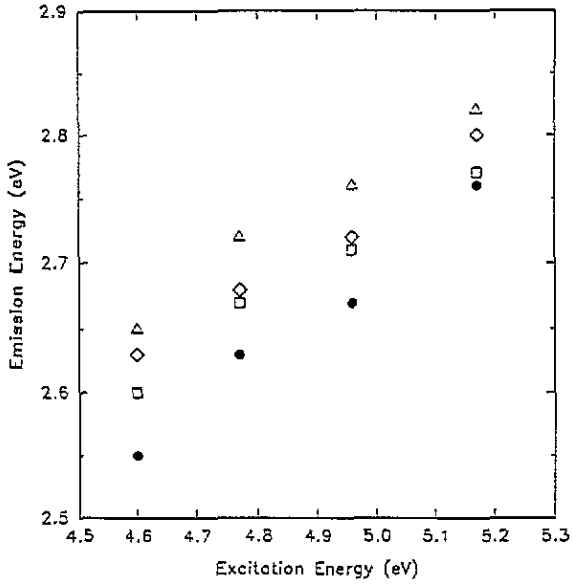

Figure 2. The emission peak energy of the γ band as a function of the exciting energy around 5 eV of a Tetrasil SE sample irradiated with 3×10^{18} neutrons cm^{-2} for different temperatures: ●, 373 K; □, 473 K; ◇, 573 K; △, 673 K.

7.7 eV, while in the same interval it is subjected to a very strong increase, with increasing temperature, for excitation at 5 eV. Under this latter excitation a quenching effect is activated at temperatures higher than 500 K.

4. Discussion

Two subjects will be discussed in the following; one regards the shifts of the emission determined by excitation energy and temperature variations and relates to electron–phonon interaction and inhomogeneous broadening; the second relates to the electron energy level model that emerges from our results.

We have found evidence for two types of shift of the position of the gamma emission peak, when exciting in the 5 eV region: we observe an increase of the emission energy both on increasing the excitation energy and on increasing the temperature in the range 200–600 K.

The former type of shift is a rather common feature in glasses and is related to the inhomogeneous broadening effect: specifically each absorption (and emission) band experimentally observed is, in reality, an envelope of peaks, each slightly different in energy due to the varying environment that the same type of centre finds in a disordered glassy structure. The excitation selects one of these centres that have slightly different absorption (and emission) energy.

As regards the unusual 'blue' temperature shift, although it is uncommon, its explanation can be found in well established theoretical analysis [10]. In particular, the temperature dependence of the absorption and emission peak position is given by $E = E_0 + \Delta E_2(T) + \Delta E_2(T)$, where E_0 is the purely electronic transition energy and $\Delta E_1(T)$ and $\Delta E_2(T)$ are the temperature-dependent harmonic and anharmonic contributions of the electron–phonon

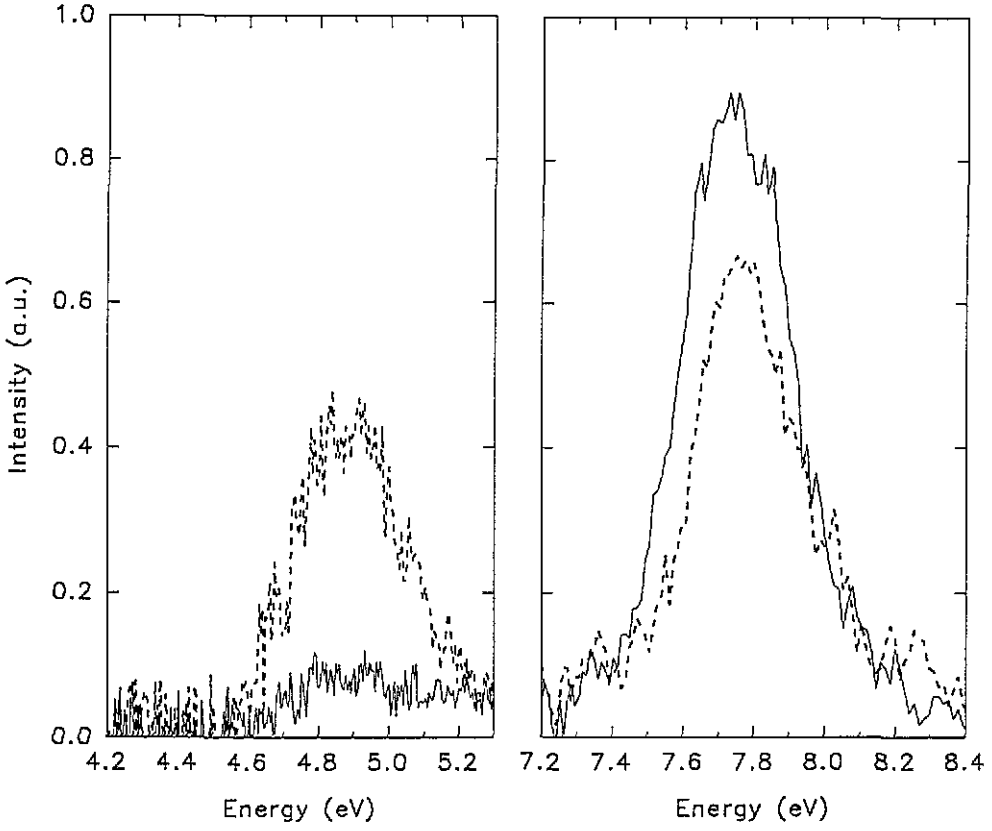

Figure 3. Excitation spectra of the 2.7 eV emission in a Tetrasil SE sample irradiated with 3×10^{18} neutrons cm^{-2}. Dashed line: $T = 300$ K, full line: $T = 90$ K

interaction. Usually these contributions are of the same order of magnitude and have the same sign, giving a red shift with increasing temperature. The different relative magnitude and sign of these terms may be responsible for the observed blue shift.

The shift of the gamma emission band as a function of temperature is not observed under VUV excitation, probably because in the temperature range in which the shift is found, the emission is quenched. That the shift of the emission peak energy is related to the exciting energy is a typical feature of the 5 eV excitation; no similar shifts have been evident under VUV excitation. We have no explanation for this at present.

A few points about the model for the centre responsible of the gamma emission should now be made, even if the data reported here do not help to decide between the two existing proposals: a twofold-coordinated silicon [2] or a neutral oxygen vacancy [3], both related to oxygen deficiency. We just propose an energy level scheme for the centre responsible of the 2.7 eV emission that explains most of the phenomenology and particularly the apparently conflicting results of a temperature-independent radiative lifetime and a strongly temperature-dependent emission intensity.

The energy level scheme reported in figure 5 consists of an excited metastable state, M, that is reached by the $\simeq 5$ eV excitation and from which radiative recombination is not allowed: let us call the number of electrons in such a state $n_{0\gamma}$, the same as the number of absorbed photons n_0. A second excited level, R, can be reached by thermal excitation

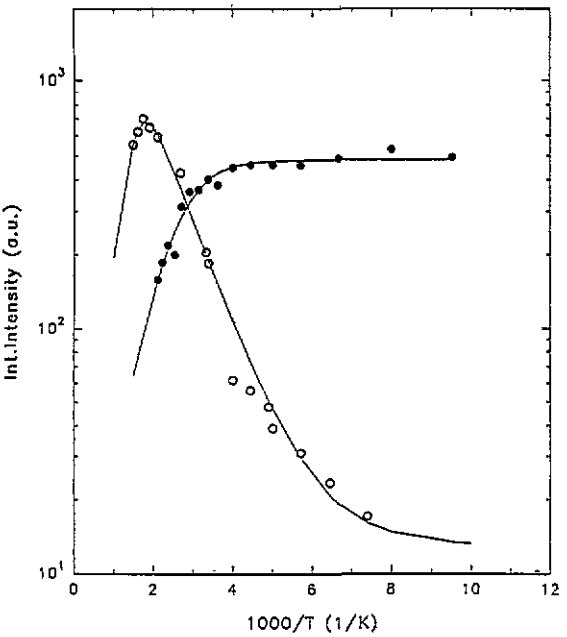

Figure 4. The temperature dependence of the integrated intensity of the γ band in a Tetrasil SE sample irradiated with 3×10^{18} neutrons cm^{-2} excited by two excitation energies: ○, 5 eV; ●, 7.7 eV. The lines are fits to the experimental data (see the text).

from the M level: let us write $n_{0R} = n_{0\gamma} \exp(-\Delta E_R/kT)$ for the number of electrons that reach R in a time $t \ll \tau$, τ being the lifetime on the level R (ΔE_R is the energy difference between levels M and R). Radiative recombination with a 10 ms lifetime is (very weakly) allowed from the R level to the ground. The increase of the emission intensity as a function of temperature is then caused by the temperature dependence of the population of the R level due to the electrons thermally excited from the M level. A fourth level, Q (the bottom of the locally perturbed conduction band?), is responsible of the quenching of the emission that is evident at temperatures greater than 600 K.

The rate of loss of electrons by the R level will be given by

$$dn_R/dt = -(1/\tau)n_R(t)$$

where $1/\tau = 1/\tau_R + 1/\tau_i = 1/\tau_R + (1/\tau_0)\exp(-\Delta E/kT)$, $1/\tau_R$ being the radiative decay probability and $1/\tau_i$ the probability of quenching occurring via a non-radiative path. $1/\tau_0$ is the frequency factor relating to the excitation of electrons from R to Q and ΔE is the energy difference between levels R and Q. Thus

$$n_R(t) = n_{0R} \exp(-t/\tau)$$

and the number of emitted photons, n_{ph}, is

$$n_{ph} = \int_0^\infty (1/\tau_R) n_{0R} \exp(-t/\tau)\, dt = (n_{0R}/\tau_R)\tau.$$

The whole mechanism can be described by a single equation in which the emission efficiency η_R is expressed as a function of the temperature, T, as follows:

$$\eta_R(T) = n_{ph}/n_0 = \exp(-\Delta E_R/kT)/[1 + (\tau_R/\tau_0)\exp(-\Delta E/kT)]. \qquad (1)$$

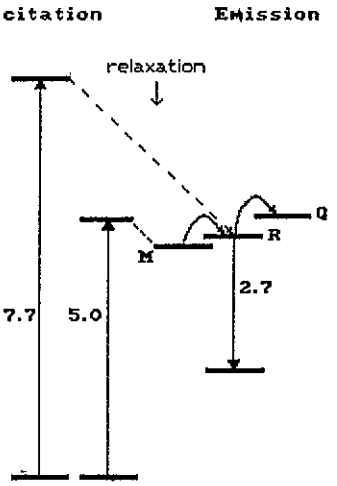

Figure 5. The proposed energy level scheme for the γ centre.

The experimental data of figure 4, relating to the intensity of the emission of the gamma band excited at 5 eV, have been fitted by the use of equation (1). The resulting curve is also reported in figure 4 and its parameters are $\Delta E_R = 0.09$ eV, $\Delta E = 0.36$ eV and $1/\tau_0 = 10^5$ s^{-1}.

The intensity of the gamma band excited at 7.7 eV has also been fitted by considering a non-radiative path that causes a quenching at $T > 300$ K. The fitted curve is also given in figure 4 together with the experimental data and its calculated slope is $\Delta E = 0.20$ eV.

Since the emission energies and radiative lifetimes are the same for 5 eV and 7.7 eV excitation, one might think that the same R level is reached in the two cases. At this point one is also led to think that ΔE should be the same, but we do not in fact obtain such a result: the value ΔE relating to 7.7 eV excitation is $\simeq 0.2$ eV and that for 5 eV excitation is $\simeq 0.36$ eV.

We then add complexity to the model, observing that at $\simeq 5$ eV we also and unavoidably excite α centres, whose emission is quenched in the temperature range in which $I(T)_\gamma$ increases. It could be assumed that the electrons ionized from the relaxed excited α centre reach (by capture from the conduction band, for example) the R level of the γ centre.

As a consequence, equation (1) contains a new contribution coming from electrons ionized into the conduction band from the α centres, n_α, and captured with a probability h into the relaxed excited state, R, of the γ centre:

$$n_\alpha = hn_{0\alpha} \exp(-\Delta E_{i\alpha}/kT)$$

where $n_{0\alpha}$ is a number of the order of $n_{0\gamma}$ (γ and α excitation–emission processes are of similar intensity) and $n_0 = n_{0\alpha} + n_{0\gamma}$. $\Delta E_{i\alpha}$ is the energy difference between the relaxed excited state responsible for the α emission and the 'ionization' level, i.e. the level from which electrons reach the γ excited level, probably through the conduction band. Then, we obtain the term

$$n_{0R} = n_{0\gamma} \exp(-\Delta E_R/kT) + hn_{0\alpha} \exp(-\Delta E_{i\alpha}/kT).$$

The new fitting lowers the value of ΔE to $\simeq 0.3$ eV, still different from the ΔE value for the 7.7 eV excitation. Further complications of the model are not proposed, to avoid speculation too far from the experimental evidence.

Let us now draw a few conclusions from our study on the 2.7 eV emission. On the experimental side, we have obtained new and detailed results on: (i) the shifts of the emission as related to the temperature and excitation energy variation; (ii) the energy distribution of the excitation and the temperature dependence of the emission excited at around 7.7 eV.

The analysis of the data has led us to propose a model that accounts for the 'anomalous' temperature dependence of the 2.7 eV emission intensity (excited to 5 eV) and for the apparent contrast between the constant lifetime and the varying emission intensity. On 7.7 eV excitation of the 2.7 eV emission we have, additionally, established that the temperature dependence different from that at 5 eV does not depend on effects due to neutrons, as earlier supposed, but we are left with a situation that is still a matter of debate. It is still doubtful if the 7.7 eV absorption transition belongs to the same centre as the $\simeq$ 5 eV absorption; a detailed analysis is prevented by the presence of overlapping absorption–excitation bands both at 5 and at 7.7 eV.

The quenching energy of the 2.7 eV emission is different for the two types of excitation. We will not understand that until we have a sound grip on the process by which the electron excited by 7.7 eV reaches the relaxed excited state from which the radiation takes place; photoconductivity studies may help to clarify this aspect.

Acknowledgment

We are grateful to Miss Barbara Crivelli for kind collaboration while preparing her undergraduate thesis.

References

[1] Garino Canina V 1954 *C. R. Acad. Sci., Paris* **238** 1577
[2] Skuja L N, Streletsky A N and Pakovich A B 1984 *Solid State Commun.* **50** 1069
[3] Tohmon R, Mizuno H, Ohki Y, Sasagane K, Nagasawa K and Hama Y 1989 *Phys. Rev.* B **39** 1337
[4] Guzzi M, Martini M, Mattaini M, Pio F and Spinolo G 1987 *Phys. Rev.* B **35** 9407
[5] Skuja L N and Entzian W 1986 *Phys. Status Solidi* a **96** 191
[6] Gee C M and Kastner M 1980 *The Physics of MOS Insulators* ed G Lukowsky, S T Pantelides and F L Galeener (New York: Pergamon) p 132
[7] Nishikawa H, Shiroyama T, Nakamura R, Ohki Y, Nagasawa K and Hama Y 1992 *Phys. Rev.* B **45** 586
[8] Stathis J H and Kastner M A 1987 *Phys. Rev.* B **35** 2972
[9] Pio F, Guzzi M, Spinolo G and Martini M 1990 *Phys. Status Solidi* b **159** 577
[10] Mulazzi E, Nardelli G F and Terzi N 1968 *Phys. Rev.* **172** 847