

The impurity levels of lanthanide ions in silica

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Abstract. Silica is a basic material of technological importance for optics, microelectronics, photonics and fibre optics and it has been used as a host material for a variety of luminescent lanthanide ions due to its chemical stability and non-hygroscopic nature. Although for lanthanide ions the 4f electron energy levels are shielded from the host environment by the filled outer 5s and 5p orbitals, making the f-f transitions relatively insensitive to the host, f-d transitions involving the unshielded 5d state are host dependent. The absolute positions of the 4f and 5d states relative to the valence and conduction bands of the host also affect quenching and charge trapping phenomena and so they are required for proper modelling of phosphor performance. Recently a model has been formulated to determine the energy levels of any of the thirteen divalent lanthanides relative to the band edges using only three host dependent parameters. Another two host dependent parameters are required to also establish the absolute levels of the trivalent ions. In this paper a scheme for the energy levels of both the divalent and trivalent lanthanide ions in silica is proposed making use of experimental data. It is suggested that although the location of the divalent europium ion f-level above the valence band can be located by using the charge transfer energy of trivalent europium, this process cannot be generalized to find the location of the trivalent cerium ion f-level above the valence band using the charge transfer energy of tetravalent cerium as has been suggested.

1. Introduction

Silica is a basic material of technological importance for optics, microelectronics, photonics and fibre optics. Its high absorption edge energy makes it particularly useful for UV applications and it has been used as a host material for a variety of luminescent lanthanide ions due to its chemical stability and non-hygroscopic nature. Specific applications include optical amplifiers doped with erbium for the telecommunications industry [1] and x-ray scintillation material doped with cerium for radiation sensing [2].

For lanthanide ions the 4f electron energy levels are shielded from the host environment by the filled outer 5s and 5p orbitals, so that the transitions between the 4f states and therefore the luminescence wavelengths are relatively insensitive to the host. For this reason little attention has been paid until recently to the location of the impurity levels of the lanthanide ions within the energy gaps of their hosts. However, luminescence from some lanthanide ions, e.g. cerium, occurs due to f-d transitions from the unshielded 5d state of which the energy relative to the f-states is therefore host dependent. The absolute positions of the 4f and 5d states relative to the energy gap of the host also affect quenching and charge trapping phenomena and so they are required for proper modelling of phosphor performance [3]. In addition, the interaction of lanthanide ions with defect levels of a host can only be studied if the energy levels of the lanthanide ions are known.

Although the use of lanthanides in luminescence phosphors became widespread about half a century ago [4], it is only recently that a phenomenological model capable of predicting the lanthanide energy levels has become available, primarily due to the work of Dorenbos - this was applied initially to CaF_2 and YPO_4 [5] and more recently to other materials e.g. GaN [6] and $\text{Al}_x\text{Ga}_{1-x}\text{N}$ [7] where it was possible to explain the lack of blue luminescence from terbium ions unless $x > 0.38$ due to overlap of the $4f^5D_3$ level with the conduction band. Only five host-specific parameters are required: the bandgap of the host and four others, two each for divalent and trivalent ions to locate the ground states of the f and the d levels respectively. In principle the data can come from any of the lanthanide ions, since the data compiled by Dorenbos [8-14] relates the values between the different lanthanide ions, but in practice usually Eu^{2+} is used for the divalent ions and Ce^{3+} for the trivalent ones, this data being the most readily obtained experimentally. However, determining the parameters to locate the levels for a particular host is not always straightforward, and in this paper a scheme for the energy levels of both the divalent and trivalent lanthanide ions in amorphous silica is proposed.

2. Model for the lanthanide impurity levels

As a first step to the model, Dorenbos [8] used experimental data to show that the differences between the f-d transition energies of trivalent lanthanide ions were independent of the host. This allowed new estimates of the free ion f-d transition energies and, using at least one experimental f-d transition energy for any trivalent lanthanide ion in a host, to give the crystal field depression $D(A,3+)$ for that host A [9]. The process was analogous for the divalent ions [10], yielding the crystal field depressions $D(A,2+)$ for divalent ions in different hosts [11].

Given the f-d transition energies E_{fd} , if one can determine either the energy from the valence band to the f-level E_{vf} or from the d-level to the conduction band E_{dc} one can place the levels absolutely. Note that

$$E_{vf} + E_{fd} + E_{dc} = E_{vc}$$

where E_{vc} is the bandgap. To first approximation, an electron promoted to the 5d level of any lanthanide ion interacts with the crystal in the same manner, since the differences between the lanthanides occurs only for the inner shielded 4f electrons. Therefore the 5d energy levels of all the lanthanides are approximately equal [5]. In addition it was found that the charge transfer (CT) energy (E^{CT}) of a trivalent lanthanide ion provides a fair measure of E_{vf} for the corresponding divalent ion [12]. By comparing small calculated changes in E_{dc} across the divalent lanthanides [13] with changes in E_{vf} based on CT data, and using the known relative f-d transition energies together with

$$\Delta E_{vf} + \Delta E_{fd} + \Delta E_{dc} = 0,$$

Dorenbos [12] was able to find the variation ΔE_{vf} across the divalent lanthanides. Then if either the f- or the d-energy level of any divalent lanthanide ion can be found relative to either the valence or the conduction band, all the f- and d-levels for all the divalent ions can be computed. The value of E^{CT} for Eu^{3+} , giving $E_{vf}(\text{Eu}^{2+})$, is often most easily obtained experimentally [14] and so ΔE_{vf} is generally expressed relative to this ion. Dorenbos [12] also predicted the variation ΔE_{vf} across the trivalent lanthanides. Although E^{CT} for tetravalent lanthanide ions is expected to be a fair measure of E_{vf} for the corresponding trivalent lanthanide ions, this data is not so readily available and so instead $E_{dc}(\text{Ce}^{3+})$ is usually estimated and for the trivalent ions ΔE_{vf} is generally expressed relative to cerium.

Therefore in addition to the bandgap of a particular host, one needs the crystal field depression of the f-d transitions and any one known absolute energy level to predict all the f- and d-levels of all the lanthanide ions. The last two parameters are needed for both divalent and trivalent ions, giving five host specific parameters in total. The free ion f-d transition energies and their relative values, together with the values of ΔE_{vf} and ΔE_{fd} are given in Table 1. Note that recently Dorenbos [15] has published new estimates of ΔE_{vf} for the divalent and trivalent ion which are used here. Older values have been

applied successfully to oxide and fluoride hosts [14], but for a sulphide host it the model did not work well and for that work the values were adapted to give a constant value for E_{dc} [16].

Table 1. Host independent data for energy level diagrams of lanthanide ions. The columns labelled Free give the f-d transition energy of the free ions. The next columns gives the relative values of the f-d energy, the energy from the valence band to the f-level ground state and the energy from the d-level ground state to the conduction band [8-15]. All values are in electron-volts.

Ion	Divalent ions, Ln^{2+} (changes relative to Eu^{2+})				Trivalent ions, Ln^{3+} (changes relative to Ce^{3+})			
	Free	ΔE_{fd}	ΔE_{vf}	ΔE_{dc}	Free	ΔE_{fd}	ΔE_{vf}	ΔE_{dc}
La	-0.94	-5.16	5.69	-0.53	-	-	-	-
Ce	0.35	-3.87	4.07	-0.20	6.12	0.00	0.00	0.00
Pr	1.56	-2.66	2.83	-0.17	7.64	1.52	-1.94	0.42
Nd	1.93	-2.29	2.50	-0.21	8.94	2.82	-3.29	0.47
Pm	1.96	-2.26	2.32	-0.06	9.31	3.19	-3.63	0.44
Sm	3.00	-1.22	1.24	-0.02	9.40	3.28	-3.74	0.46
Eu	4.22	0.00	0.00	0.00	10.58	4.46	-4.92	0.46
Gd	-0.10	-4.32	4.67	-0.35	11.81	5.69	-6.17	0.48
Tb	1.19	-3.03	3.23	-0.20	6.97	0.85	-0.88	0.03
Dy	2.12	-2.10	2.30	-0.20	8.58	2.46	-2.53	0.07
Ho	2.25	-1.97	2.44	-0.47	9.72	3.60	-3.55	-0.05
Er	2.12	-2.10	2.62	-0.52	9.46	3.34	-3.41	0.07
Tm	2.95	-1.27	1.77	-0.50	9.46	3.34	-3.18	-0.16
Yb	4.22	0.00	0.49	-0.49	10.83	4.71	-4.15	-0.56
Lu	-	-	-	-	12.22	6.10	-5.64	-0.46

3. Lanthanide impurity levels in amorphous silica

Amorphous silica samples doped with lanthanide ions were prepared with the sol-gel process using TEOS as a precursor and annealed at 1000°C. Emission and excitation measurement were performed on a Cary Eclipse fluorescence spectrophotometer having a xenon lamp as well as with synchrotron radiation using the SUPERLUMI station of HASYLAB at DESY. All measurements were made at room temperature, and excitation spectra from SUPERLUMI were corrected for the incident flux by comparison to the excitation spectrum of sodium salicylate.

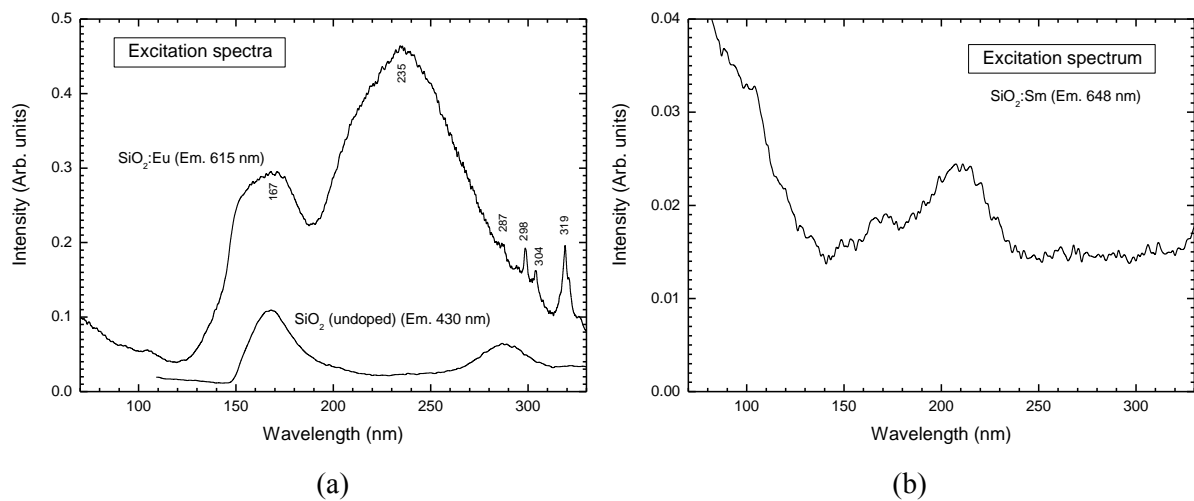


Figure 1. Excitation spectra for sol-gel silica measured at SUPERLUMI. (a) undoped and Eu doped silica (b) Sm doped silica.

Fig 1(a) shows the excitation spectrum of a sample doped with 1% Eu while monitoring the emission due to Eu^{3+} ions at 618 nm. The small sharp features around 300 nm are due to f-f transitions of Eu^{3+} [17], while the broad band at 235 nm (5.28 eV) is the CT band. A similar excitation spectrum was obtained by Yi *et al.* [18], but they only measured down to 250 nm. The band near 170 nm was also observed in undoped silica as well as when doping with different lanthanides and is attributed to defects in the silica [19]. The value of $E^{\text{CT}}(\text{Eu}^{3+})$ is used for the energy $E_{\text{Vf}}(\text{Eu}^{2+})$ and from the differences in Table 1, the absolute f-levels of the divalent lanthanide ions are established as in Fig. 2(a). The value found here agrees well with that for silicates listed by Dorenbos [14]. From Fig. 2(a) one may predict that $E^{\text{CT}}(\text{Eu}^{3+})$ will lie 1.24 eV above that of Eu^{3+} at 6.51 eV (190 nm). Recently Gutsov *et al.* [20] attributed a broad absorption peak in Sm doped sol-gel silica at 35714 cm^{-1} (4.42 eV, 280 nm) to $E^{\text{CT}}(\text{Sm}^{3+})$. However, this energy lies lower than that for Eu^{3+} and is not consistent with our results. Fig. 1(b) shows the excitation spectrum of $\text{SiO}_2:\text{Sm}$ and the CT band is found at 210 nm, fairly close to the 190 nm predicted from the model. An excitation band near 280 nm, similar to that found by Gutsov *et al.* [20], is also found for undoped silica (Fig. 1(a)) and may be associated with defects [19].

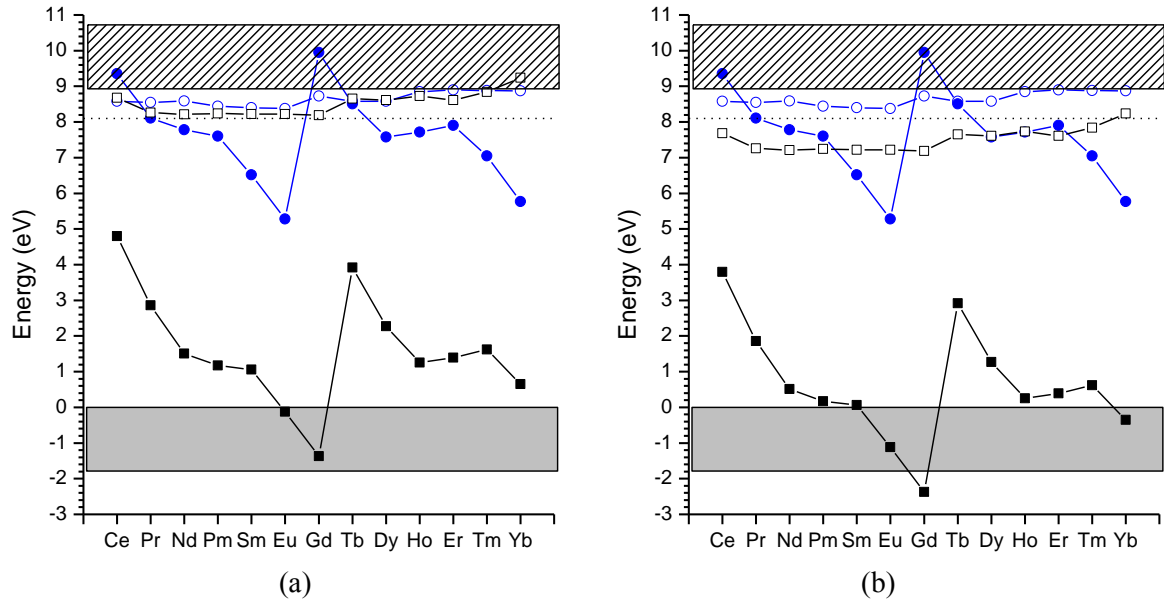


Figure 2. Location of the energy levels of divalent and trivalent lanthanide ions in silica. (a) Scheme based on associating $E^{\text{CT}}(\text{Ce}^{4+})$ with the value $E_{\text{Vf}}(\text{Ce}^{3+})$. (b) More realistic scheme obtained by reducing $E_{\text{Vf}}(\text{Ce}^{3+})$ in (a) by 1 eV.

To obtain the divalent lanthanide d-levels, the crystal field depression $D(A,2+)$ is required, but this value is not given for silica in the extensive tabulations of Dorenbos [11]. Hu *et al.* [21] give an excitation spectrum for Eu^{2+} f-d luminescence near 450 nm from sol-gel silica. Since the lowest d-level overlaps with higher levels the excitation peak value should not be used, but rather the 15-20% onset value on the long wavelength side [11], which is about 400 nm (3.1 eV). Comparing this to the free ion value of 4.22 eV gives $D(A,2+) = 1.12 \text{ eV}$, from which all the f-d transition energies and hence the d-levels can be calculated, as shown in Fig. 2(a).

Although Ce^{4+} is non-luminescent, absorption experiments can be used to determine its CT band, and a value of about 260 nm (4.8 eV) has been reported [22-23]. If $E^{\text{CT}}(\text{Ce}^{4+})$ is interpreted as $E_{\text{Vf}}(\text{Ce}^{3+})$ then the absolute f-levels of the trivalent lanthanide ions can be determined. However, there are some indications that this is not the case. Firstly, let us consider the d-levels of the trivalent ions based on this value. To do so we require $D(A,3+)$, which can be obtained by comparing an f-d transition energy in silica with that of the free ion listed in Table 1. Fig 3(a) shows the luminescence spectra of trivalent

Ce^{3+} in silica. The excitation maximum occurs near 320 nm (3.88 eV), giving $D(A,3+) = 2.24$ eV, from which the d-levels can be derived as shown in Fig. 2(a). Here the d-levels of the trivalent ions lie about equal in energy to the divalent ones, whereas they should lie slightly lower. Dorenbos [9] does tabulate a value of $D(A,3+)$ for silica, but we believe our value is more accurate since in the reference used by him the sample had not been annealed at high temperature to incorporate the cerium in the silica. To further check the value, consider the excitation spectrum of a sample doped with Tb while monitoring the emission due to Tb^{3+} ions at 545 nm (Fig. 3(b)). The peak at 226 nm (5.49 eV) is the f-d absorption band, while the peak near 160 nm is due to defects as mentioned before. This f-d energy cannot, however, be compared directly to that of the free ion because the lowest f-d transition for Tb^{3+} is spin-forbidden. The experimental value corresponds to the first spin-allowed f-d transition which occurs 0.78 eV higher [8,24]; therefore the crystal field depression can be estimated as $(6.97 + 0.78) - 5.49 = 2.26$ eV, in excellent agreement with the value from cerium. Additionally, Dorenbos [25] has shown that the crystal field depressions for divalent and trivalent ions are related by $D(A,2+) = 0.64D(A,3+) - 0.233$, which holds reasonably well for the values obtained here. It therefore appears that the crystal field depression is accurate, so the higher than expected trivalent d-levels seem to be as a result of overestimation of $E_{\text{Vf}}(\text{Ce}^{3+})$. A second factor that seems to indicate this is the difference in the f-levels of trivalent and divalent Eu: generally it varies from above 7 eV in poorly polarisable compounds like the fluorides to below 6 eV in strongly polarisable compounds like bromides and sulphides, and for the metal it is 5.4 eV [15]. In the model of Fig. 2(a) it is only 5.4 eV, and a realistic value is at least 1 eV higher. Decreasing $E_{\text{Vf}}(\text{Ce}^{3+})$ to 3.8 eV achieves this and also brings the trivalent 5d levels 1 eV below the divalent ones, creating the more realistic energy structure in Fig. 2(b). Since we have no reason to doubt the accuracy of the Ce^{4+} CT absorption energy (or any of the other measurements) to the extent of the correction applied, it is concluded that the value of $E_{\text{Vf}}(\text{Ce}^{3+})$ cannot be associated with the Ce^{4+} CT absorption energy. Although using the CT absorption energies of tetravalent ions was suggested initially [12], to our knowledge it has not been applied before and generally a value of $E_{\text{dc}}(\text{Ce}^{3+})$ is estimated instead. It has been acknowledged that identifying the trivalent CT energies with the absolute energies of the divalent ions above the valence band is an assumption that can be disputed [15], and although it appears to work well to find values of $E_{\text{Vf}}(\text{Eu}^{2+})$, in this work we have shown that a similar method is not as successful for determining $E_{\text{Vf}}(\text{Ce}^{3+})$.

To complete the energy level diagrams in Fig. 2 only the bandgap of amorphous silica is required. This has been determined as 9.0 eV by photoconductivity measurements [26], with the fundamental absorption edge at 8.1 eV [27] shown by a dotted line in Fig. 2.

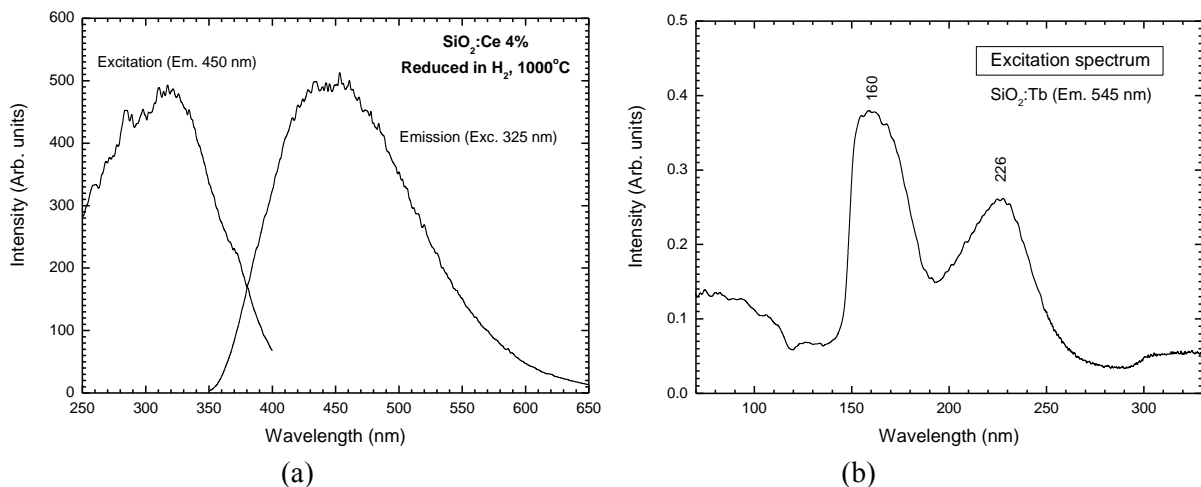


Figure 3. (a) Excitation and emission spectra of 4% Ce doped silica after annealing in reducing atmosphere at 1000°C for 2 h, measured with Cary Eclipse. (b) Excitation spectrum of 0.1% Tb doped silica measured synchrotron radiation and SUPERLUMI.

References

- [1] Tanabe S 2005 *IPAP Books* **2** 101
- [2] Chiodini N *et al.* 2009 *Proc. SPIE* **7136** 731614
- [3] Dorenbos P 2007 Lanthanide level locations and its impact on phosphor performance. *Phosphor Handbook* 2nd ed. ed W M Yen, S Shionoya and H Yamamoto (Boca Raton: CRC Press) p 139
- [4] Dorenbos P and Bos AJJ 2008 *Rad. Meas.* **43** 139
- [5] Dorenbos P 2004 *J. Lumin.* **108** 301
- [6] Dorenbos P and van der Kolk E 2006 *Appl. Phys. Lett.* **89** 061122
- [7] Dorenbos P and van der Kolk E 2008 *Opt. Mat.* **30** 1052
- [8] Dorenbos P 2000 *J. Lumin.* **91** 91
- [9] Dorenbos P 2000 *J. Lumin.* **91** 155
- [10] Dorenbos P 2003 *J. Phys: Condens. Matter* **15** 575
- [11] Dorenbos P 2003 *J. Lumin.* **104** 239
- [12] Dorenbos P 2003 *J. Phys: Condens. Matter* **15** 8417
- [13] Dorenbos P 2003 *J. Phys: Condens. Matter* **15** 2645
- [14] Dorenbos P 2005 *J. Lumin.* **111** 89
- [15] Dorenbos P 2009 *J. alloys and compounds* **488** 568
- [16] Bressiere A, Dorenbos P, van Eijk CWE, Yamagishi E, Hidaka C and Takizawa T 2004 *J. Electrochem. Soc.* **151(12)** H254
- [17] Carnall WT 1979 The absorption and fluorescence spectra of rare earth ions in solution. *Handbook on the Physics and Chemistry of Rare Earths* vol 3 ed K A Gschneider Jr and L Eyring (Amsterdam: North Holland) p 171
- [18] Yi W, Lansheng L, Huiqun Z and Ruiqin D 2006 *J. Rare Earths* **24** 199
- [19] Sakurai Y and Nagasawa K 2001 *J. Non-Cryst. Solids* **290** 189
- [20] Gutzov S, Ahmed G, Petkova N, Fügleinand E and Petkov I 2008 *J. Non-Cryst. Solids* **354** 3438
- [21] Hu X, Fan J, Li T, Zhang D, Chen W, Bai J and Hou X 2007 *Opt. Mat.* **29** 1327
- [22] Patra A, Kundu D and Ganguli D 1997 *J. Sol-Gel Sci. Techn.* **9** 65
- [23] Fasoli M, Vedda A, Lauria A, Moretti A, Rizzelli E, Chiodini N, Meinardi F and Nikl M 2009 *J. Non-Cryst. Solids* **355** 1140
- [24] Dorenbos P 2003 *J. Phys: Condens. Matter* **15** 6249
- [25] Dorenbos P 2003 *J. Phys: Condens. Matter* **15** 4797
- [26] DiStefano TD and Eastman DE 1971 *Solid State Comm.* **9** 2259
- [27] Guzzi M, Martini M, Paleari A, Pio F, Vedda A and Azzoni CB 1993 *J. Phys: Condens. Matter* **5** 8105