JOURNAL OF MATERIALS SCIENCE 27 (1992) 6352–6356

Optical properties of O_2^- centres in KCl:NaCl mixed crystals

T. KUROBORI
Department of Material Science and Engineering, Kanazawa University, 1-1 Marunouchi, Kanazawa 920, Japan

S. TANIGUCHI, N. TAKEUCHI
Faculty of Technology, Kanazawa University, 2-40-20 Kodatsuno, Kanazawa 920, Japan

The optical properties of O_2^- centres in KCl:NaCl mixed crystals were investigated. The time-resolved spectra and the fluorescence decay time are shown. From the measurements of the radiative decay time, the oscillator strength of the absorption, $f_{ab} = 0.045$, the oscillator strength of the fluorescence, $f_{fluo} = 0.019$, and the activation energy $\Delta E = 0.22$ eV for the O_2^- centre in KCl:NaCl were determined.

1. Introduction

Since the observation of superradiance at temperatures below 30 K [1] and laser action at 77 K [2], the O_2^- centres in alkali halide crystals have attracted much attention as possible candidates for active materials in tunable visible lasers, although there are serious obstacles to their use as practical light sources.

The optical spectra and the structure of O_2^- centres in alkali halide crystals have been investigated in detail by Rolfe *et al.* [3], Känzig [4] and Rolfe [5]. Recently, optical properties, especially studies of the relaxation time in the excited state [6] and the fluorescence decay time [7], have been investigated in several host crystals such as KCl, KBr, KI, RbCl, RbBr, NaCl and NaBr. One of the most prominent features in the optical spectra is that the O_2^- centre in KCl, RbCl, RbI and RbBr has its molecular axis along the ⟨110⟩ direction and shows double structure phonon sidebands, while the O_2^- centre in NaCl, KI, KBr and NaBr has its molecular axis along the ⟨1 1 1⟩ direction and shows single structure sidebands. Several attempts to determine the reason for this difference have been made using the level schemes and transition [7, 8] and polarized Raman spectroscopy [9].

In order to clarify the difference which stems from the different host crystals, we first investigated how the O_2^- centre in KCl:NaCl mixed crystals behaves in comparison to that in a single host crystal. The KCl:NaCl mixed crystal was selected because both the behaviour and optical parameters, such as the fluorescence decay time of the O_2^- centre in a KCl host crystal, are quite different from those in an NaCl host crystal. Further investigation of the optical properties enables us to obtain additional and more detailed information about the ground-state, and excited-state in KCl:NaCl:O_2^- and to give a suggestion of stable laser action with the O_2^- centre in alkali halide crystals. In this paper we briefly report some preliminary results on the time-resolved spectra and the fluorescence decay time in KCl:NaCl:O_2^- mixed crystals. In addition, the oscillator strength of the absorption, the oscillator strength of the fluorescence and the activation energy of the O_2^- centre in KCl:NaCl mixed crystals are determined from the radiative decay time.

Such a mixed crystal has been applied to the $(F_2^+)_{AH}$ centres in KCl:NaCl:O_2^- [10] and the $F_A(II)$ centres in KCl:RbCl:Li crystal [11] to obtain efficient and stable laser action, as well as enlargement of the emission range.

2. Experimental procedure

The crystals were grown under a partial oxygen atmosphere from a melt containing about 5×10^{-4} mol % KO_2 and about 10^{-2} mol % NaCl, and cleaved to samples of about $10 \times 10 \times 2$ mm^3. The concentrations in the preparation were the same as those used for the laser action with the KCl:NaCl:O_2^- $(F_2^+)_{AH}$ centre [10]. In order to enhance the effects of Na^+ cations as additional perturbation to the O_2^- centre, the concentration was as high as possible. However, the KCl:NaCl system cannot form a solid solution through the composition range. The measured absorption and excitation spectra in the ultraviolet are shown in Fig. 1. The absorption spectrum was measured with a Hitachi U-2000 spectrophotometer, while the excitation and emission spectra were measured with a Hitachi F-3010 spectrofluorometer. As the absorption due to oxygen was small, the 5.29 mm thick KCl:NaCl:O_2^- crystal was used to measure the absorption spectrum. The absorption spectrum consists of two absorption bands with a maximum absorption at 204.0 and 243.5 nm at room temperature. The former is due to the OH^- centres and the latter is due to the O_2^- centres, respectively. The peak wavelengths for these centres are in good agreement with those reported for KCl:O_2^- crystals [12]. The OH^- and O_2^- concentrations of the crystals were determined by measuring the optical absorption coefficient [12] and estimated to be about 2.1×10^{17} cm^{-3} and 3.1×10^{17} cm^{-3}, respectively. The O_2^- concentrations were almost the same as those used for the observation of superradiance [1] and the laser action in KCl:O_2^- [2].

The measurements of the radiative decay time were performed by a time-resolved spectrofluorometer (Horiba Ltd, NAES-1100) which was based on the time-correlated photon counting technique. An outline of the apparatus was given previously [13, 14]. The sample was mounted on the cold head in an Oxford variable temperature cryostat (DN-1754) in conjunction with an Oxford temperature controller (ITC-4). The temperature was stabilized to within ± 0.1 K. Both exciting and emitting wavelengths were monochromatized and observed by the use of two monochromators and appropriate filters. The pulse width (FWHM) of a high-pressure flash lamp was less than 2 ns and the repetition rate was about 6 kHz. The exciting light was set at a wavelength of 260 nm, which is the peak wavelength for the excitation spectrum as shown in Fig. 1. At room temperature the emission spectrum consists of nine or ten peaks, which are almost equally spaced in energy. The separation is about 1000 cm^{-1}. At lower temperature, as already reported in detail, each peak at room temperature splits into two large peaks each with fine structure. As far as both the structure of the emission spectrum and the peak wavelength of the absorption are concerned, it seems that the effects of the doped Na^+ impurities are almost negligible. However, the peak position of the emission spectrum, as listed in Table I, was different from that of the reported results for KCl:O_2^- and NaCl:O_2^- [3]. That is, in the regions of the wavelength around 540 nm, each peak position fits in with that of the NaCl:O_2^-, while in the regions of both shorter and longer wavelengths than 540 nm, each peak position fits in with that of KCl:O_2^-. At present the reason for this is not clear.

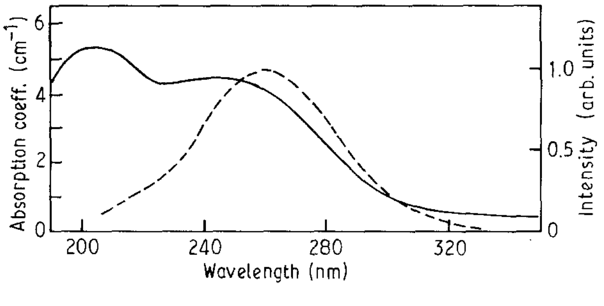

Figure 1 (——) Absorption and (– – –) excitation spectra of O_2^- centres in KCl:NaCl measured at room temperature. Crystal thickness 5.29 mm.

TABLE I Fluorescence emission spectra at 300 K.

KCl:NaCl			NaCl [3]	KCl [3]
Wavelength (nm)	Wave number (cm^{-1})	Difference (cm^{-1})	wavelength (nm)	wavelength (nm)
441.0	22676		439.6	440.4
		1143		
464.4	21533		461.8	462.9
		1008		
487.2	20525		486.1	485.4
		1009		
512.4	19516		512.6	510.9
		997		
540.0	18519		540.1	538.1
		994		
570.6	17525		570.6	568.6
		947		
603.2	16578		605.3	601.8
		943		
639.6	15635		642.7	639.8
		929		
680.0	14706		685.6	681.2

3. Results and discussion

The typical fluorescence decay curves measured at a set of different temperatures are shown in Fig. 2. These curves (a–d) were obtained by excitation into the 260 nm band and by detection, at the maximum wavelength of 570 nm, of the emission band. Curve (e) shows the excitation waveform. It is found that these curves are always purely single exponential over nearly four orders of magnitude in time and do not depend on the wavelength of observation. As can be seen in this figure, at 77 K the decay time, τ, is 85.0 ns for the sample with an O_2^- concentration of 3.1×10^{17} cm^{-3}. When raising the temperature, τ decreases slowly to about 80.7 ns at 200 K and drops more steeply to 30.1 ns at 330 K. Parallel to this decrease in τ, the intensity of the fluorescence emission also decays.

From the radiative decay time, τ_r, we can determine the oscillator strength of the fluorescence, f_{fluo}, from the well-known formula

$$f_{\text{fluo}} = \frac{1}{8\pi^2}\left(\frac{\lambda^2}{cr_0\tau_r}\right)\left\{\frac{1}{n[(n^2+2)/3]^2}\right\} \tag{1}$$

where c is the speed of light, r_0 the classical electron radius, λ the oscillating wavelength and n the index of refraction of the host. For $\tau_r = 85$ ns at 77 K, $\lambda = 570$ nm at the centre of the emission and $n = 1.49$, Equation yields $f_{\text{fluo}} = 0.019$.

Furthermore, we can also estimate the oscillator strength of the absorption, f_{ab}, from the Fowler–Dexter formula [15]. The Fowler–Dexter formula can be written more simply [14] as

$$f_{\text{ab}} = \frac{23.05}{\tau_r}\left(\frac{1}{n}\right)\left(\frac{3}{n^2+2}\right)^2\left(\frac{E_{\text{ab}}}{E_{\text{em}}^3}\frac{2J_k+1}{2J_m+1}\right) \tag{2}$$

where τ_r is the radiative decay time (ns) and f_{ab} the oscillator strength of the absorption. E_{ab} and E_{em} are the transition energies for absorption and emission (eV), respectively, $J_{m,k}$ is the degeneracy factor, in which the subscripts m and k denote the fundamental and the excited states, respectively, n is the refractive index. The estimation was also performed assuming that the electric matrix elements for absorption and emission were equal to unity. For $\tau_r = 85$ ns at 77 K, $E_{\text{ab}} = 5.08$ eV, $E_{\text{em}} = 2.18$ eV, $n = 1.49$, Equation 2 yields $f_{\text{ab}} = 0.045$.

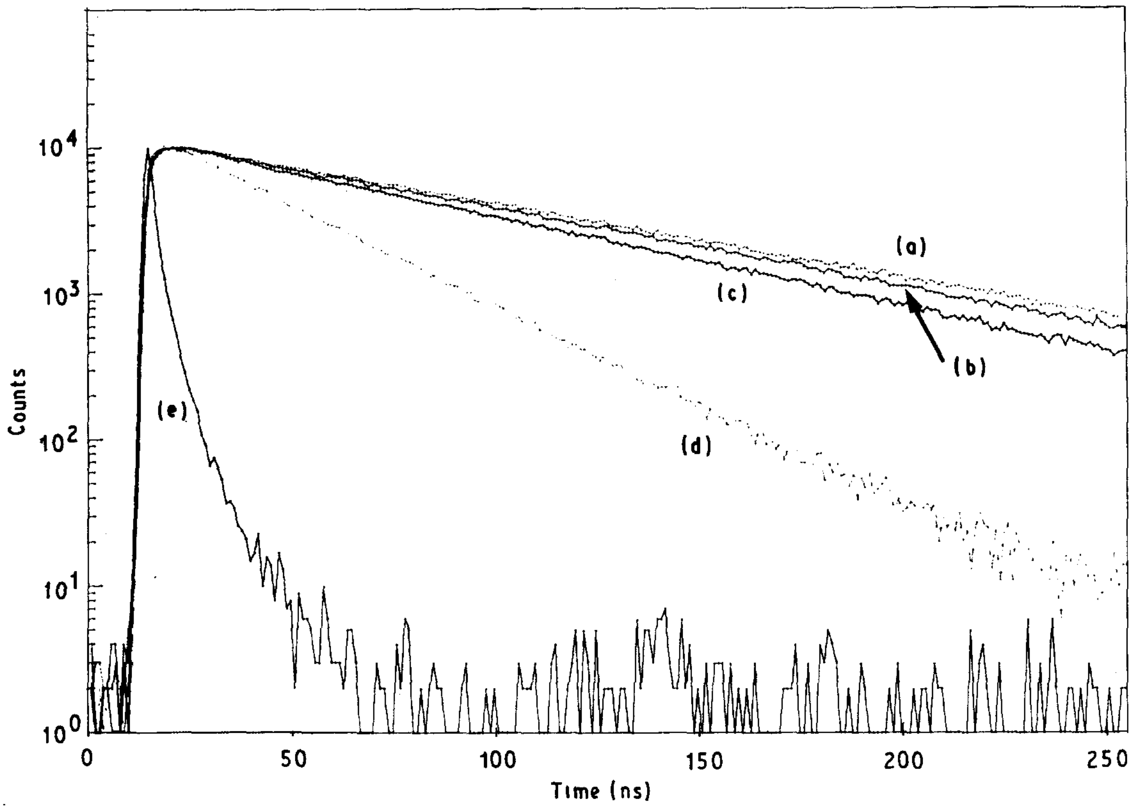

Figure 2 Decay curves of O_2^- centres in KCl:NaCl, measured at (a) 77 K, (b) 200 K, (c) 250 K and (d) 330 K. (e) The excitation pulse waveform. Excited at 260 nm; detected at 570 nm.

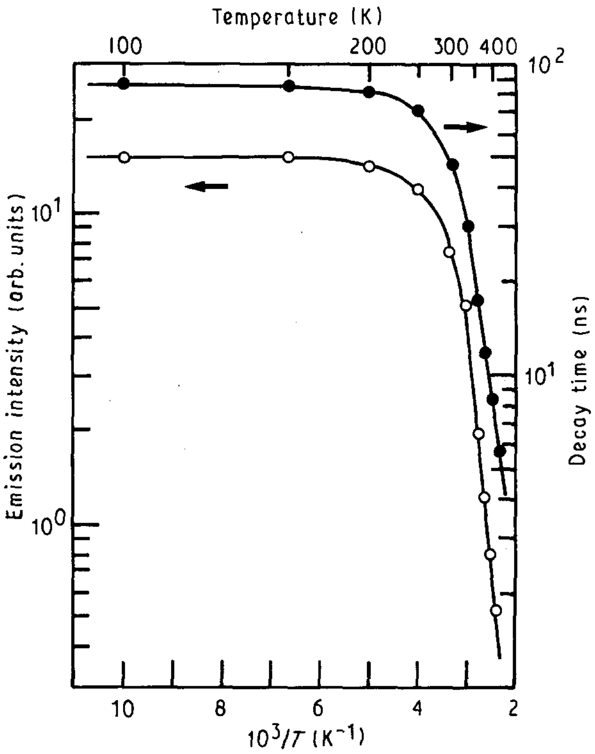

Figure 3 Temperature dependence of (●) decay time and (○) intensity of the fluorescence in KCl:NaCl:O_2^-.

The decay time, τ, of the fluorescence in KCl:NaCl:O_2^- are plotted as a function of T^{-1} in Fig. 3. This trend agrees well with the experimental results reported for KCl:O_2^- crystals [7], though the decay time values obtained here for the KCl:NaCl mixed crystal are slightly different from that of KCl:O_2^- (80 ns) and quite different from that of NaCl:O_2^- (9 ns). The rapid decline of the decay curves in the high-temperature range, which correlates with diminishing intensity of fluorescence emission, reflects the dominance of competing non-radiative de-excitation processes. The temperature dependence of τ is described by

$$\tau^{-1} = \tau_r^{-1} + \tau_{nr}^{-1}\exp(-\Delta E/kT) \qquad (3)$$

where τ is the observed decay time, τ_r radiative decay time, τ_{nr} nonradiative decay time and ΔE the activation energy of a competitive de-excitation thermal process. From the usual phenomenological relation, we obtained $\Delta E = 0.22$ eV. The value of ΔE calculated here agrees well with the value, $\Delta E = 0.25$ eV, for KCl:O_2^- and NaCl:O_2^- crystals [8].

Fig. 4 shows the time-resolved spectra measured at 5 ns intervals after irradiation of the exciting pulses for KCl:NaCl:O_2^- crystals at 290 K. It can be seen from this figure that the maximum intensity of the fluorescence was about 25 ns after irradiation of the exciting pulses. The three-dimensional graphs of time- and wavelength-dependent fluorescent intensities were obtained by reconstructing the analysis data of time-resolved decays of fluorescence intensity at variable wavelengths, as shown in Fig. 5.

4. Conclusion

The optical properties of the O_2^- centres in KCl:NaCl mixed crystal are reported. The influence of Na^+ impurities as additional perturbation to the O_2^- centre was too small to change the optical parameters such as the fluorescence decay times and the activation

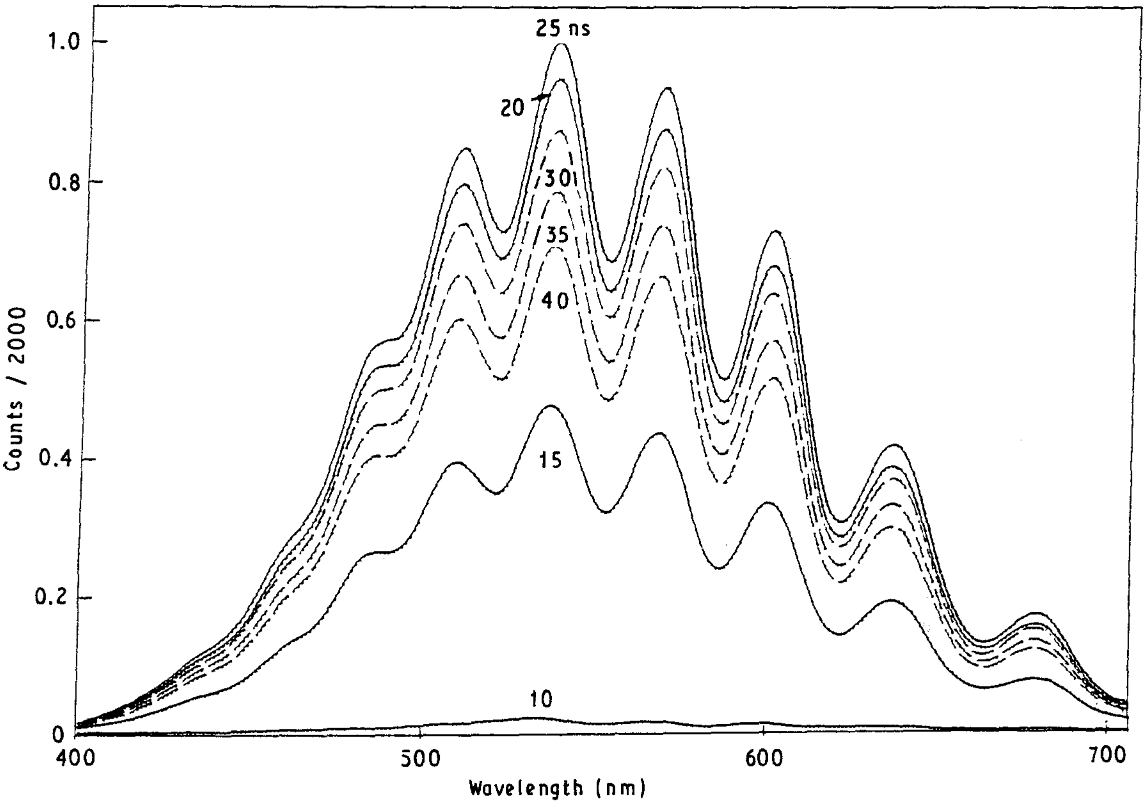

Figure 4 Time-resolved spectra measured at 5 ns intervals for KCl : NaCl : O_2^- at room temperature.

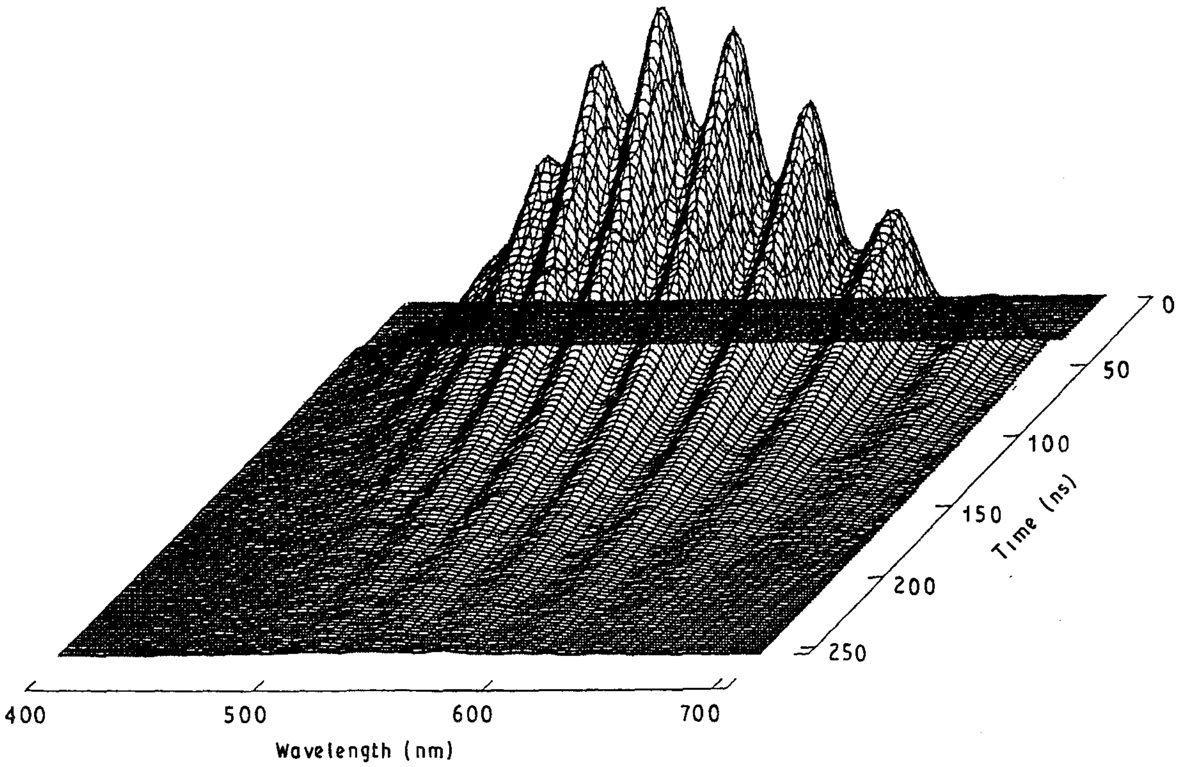

Figure 5 Three-dimensional fluorescence spectra for KCl : NaCl : O_2^- at room temperature.

energies. From the measurements of the radiative decay time, we could determine the oscillator strength of the absorption, $f_{ab} = 0.045$, the oscillator strength of the fluorescence, $f_{fluo} = 0.019$, and the activation energy $\Delta E = 0.22$ eV for the O_2^- centre in KCl : NaCl mixed crystal. As already pointed out [2], the laser emission of KCl : O_2^- at 77 K died away after several shots due to destruction of the active O_2^- centres under intense pump radiation. The Na^+ impurities doped as additional perturbation to the O_2^- centre, seem to play a role in the long operating lifetime of the laser action in comparison to the single host crystal. The laser action of the KCl : NaCl : O_2^- mixed crystal pumped by a KrF excimer laser is currently under investigation. Furthermore, the optical properties of the O_2^- centres in KCl : KBr system, which forms a solid solution through the composition range, are also being investigated.

References

1. R. FLORIAN, L. O. SCHWAN and D. SCHMID, *Solid State Commun.* **42** (1982) 55.
2. S. R. WILK, R. W. BOYD and K. J. TEEGARDEN, *Opt. Commun.* **47** (1983) 404.
3. J. ROLFE, F. R. LIPSETT and W. J. KING, *Phys. Rev.* **123** (1961) 447.
4. W. KÄNZIG, *J. Phys. Chem. Solids* **23** (1962) 479.
5. J. ROLFE, *J. Chem. Phys.* **40** (1964) 1664.
6. L. O. SCHWAN, R. FLORIAN, D. SCHMID, E. BETZ, W. SCHROF, B. WALKER and H. PORT, *Phys. Status Solidi (b)* **124** (1984) 741.
7. S. HONGO, H. MURATA and R. KATO, *J. Luminescence* **48, 49** (1991) 807.
8. G. J. VELLA and J. ROLFE, *J. Chem. Phys.* **61** (1974) 41.
9. H. FLEURENT, W. JOOSEN and D. SCHOEMAKER, *Phys. Rev. B* **38** (1988) 6257.
10. D. WANDT and W. GELLERMAN, *Opt. Commun.* **61** (1987) 405.
11. K. P. KOCH, G. LITFIN and H. WELLING, *Opt. Lett.* **4** (1979) 387.
12. F. FISCHER, H. GRÜNDIG and R. HILSCH, *Z. Physik* **189** (1966) 79.
13. T. KUROBORI, Y. IMAI and N. TAKEUCHI, *Opt. Commun.* **64** (1987) 259.
14. T. KUROBORI, T. KANASAKI, Y. IMAI and N. TAKEUCHI, *J. Phys. C.* **21** (1988) L397.
15. W. B. FOWLER and D. L. DEXTER, *Phys. Rev.* **128** (1962) 2154.

Received 26 June 1991
and accepted 4 February 1992