Luminescence properties of solids
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Recent advances have been made in research on the luminescence of solids. The areas which have received particular attention have been transition metal ion systems, upconversion systems, high-resolution spectroscopy and single molecule spectroscopy, scanning near-field optical microscopy, new scintillator materials and luminescence of silicon. The applied research is focused on opto-electronic applications of new luminescent materials. In addition, single molecule spectroscopy gives new insight into many fundamental aspects of physics and chemistry.

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Abbreviations
SHB   spectral hole burning
SMS   single molecule spectroscopy
SNOM   scanning near-field optical microscopy

Introduction

During the period from January 1994 to October 1995 interesting and sometimes exciting research was reported in the field of luminescence of solids. A large part of the research is currently stimulated by opto-electronic applications of luminescent materials, such as lasers, displays and optical storage media. As the field is very broad and active, it would be impossible to review all facets here. Instead, we have chosen to review some areas which have been particularly active or innovative over the past year. These include transition metal ion systems, upconversion systems, high-resolution spectroscopy and single molecule spectroscopy, scanning near-field optical microscopy, new scintillator materials and luminescence of silicon. A good introduction to the field is provided in reference [1].

Transition metal ion systems

Luminescent materials doped with transition metal ions can be used as laser materials. The laser wavelength can be tuned for the laser material chromium doped Mg_2SiO_4 (Cr:forsterite) which shows near infrared (NIR) luminescence. This luminescence has recently been unambiguously assigned to a spin-allowed transition of the Cr^{4+} ($3d^2$) ion in tetra-oxo coordination [2•,3•]. The understanding of non-radiative processes is very important for development of laser materials [1]. The phonons participating in the non-radiative relaxation of $Cr:Mg_2SiO_4$ have been directly measured using fast, time-resolved Raman spectroscopy [4]. The NIR luminescence of other first-row transition metal ions in tetra-oxo coordination is currently being studied as well. In addition to the $3d^2$ ions Mn^{5+} and Fe^{6+}, which show sharp line luminescence, the Mn^{6+} ion ($3d^1$) is very interesting [5•]. Its luminescence band extends from 7000–$11\,000\,cm^{-1}$; it has a rich vibrational structure (Fig. 1); and in some host lattices the luminescence persists up to room temperature. Hence, Mn^{6+} doped systems have potential applications as tunable NIR laser materials.

The optical spectroscopic properties of transition metal ions in complexes are being studied with more and more sophisticated methods. Riesen and Krausz [6•] investigated the $[Ru(bipy)_3]^{2+}$ complex in the solid state using fluorescence line narrowing and spectral hole burning techniques under various perturbations. They proved that for $[Ru(bipy)_3]^{2+}$ doped into solids at $1.8\,K$ the excited electron is localized on one of the three bipy ligands in the lowest excited metal to ligand charge transfer state. In contrast, Yersin and co-workers [7] arrived at the opposite conclusion, namely a delocalized excited state for the same system at $1.8\,K$.

Improved models and faster computers allow a theoretical modelling of excited state properties of solid state luminescent materials. Several *ab initio* studies have been published which give very reasonable descriptions of relaxed excited states (i.e. electronic excited states which are vibrationally relaxed). Correspondingly, the agreement between experimental results on absorption and luminescence bands is good (e.g. the density functional study in [8] and the embedded cluster calculations in [9]). In a very interesting study in this area, non-radiative relaxation rates of Cr^{3+} doped laser materials were calculated with a totally *ab initio* approach [10•]. The results are in reasonable agreement with those from experiments, and this opens new perspectives in the design of new luminescent materials.

Wexler, Zink and Reber [11] have extended the time-dependent theory of luminescence and absorption spectroscopy by introducing coupling between vibrational coordinates. For example, this model can be applied to understand the unusual vibrational structure in the luminescence spectrum of solid *trans*-[ReO_2(1-methylimidazole)_4]I [12], which arises from the coupling between two different vibrational modes. This study shows the first example of coupling between two metal–ligand modes involving different ligands; in this case the Re–O and the Re–N stretching vibrations.

Figure 1

Luminescence spectrum at 10 K of $MnO_4{}^{2-}$ doped K_2SO_4 upon excitation at 17600 cm⁻¹. The two electronic transitions I and II are indicated in the figure and assigned in the inset. The vibrational progressions are labelled v_α, v_β, v_γ for the bending vibrations and v_1 for the stretching vibration. A' and A" are the term symbols in the point group C_s. (Published with permission from [5•].)
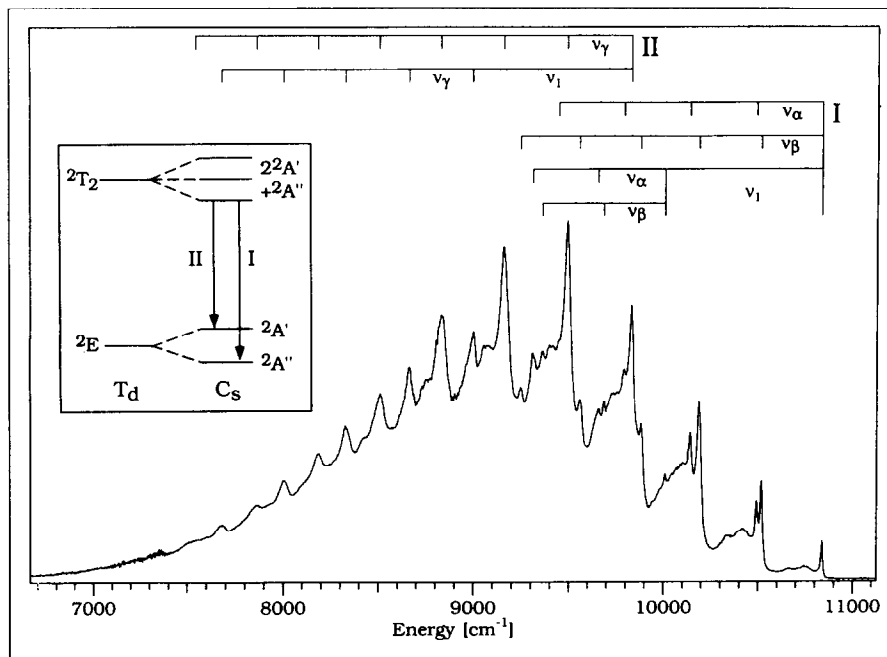
Upconversion systems

During the review period many papers were published on rare earth doped crystals, glasses and fibres, which show visible luminescence upon red or infrared excitation (i.e. upconversion). These materials may be used for diode pumped solid state visible lasers. A green upconversion laser at room temperature, based on Er^{3+} doped $LiYF_4$, has recently been reported [13•]. This was the first green emitting room-temperature continuous-wave laser using an Er^{3+} doped crystal. The achievement of laser action in a crystal at room temperature is very important for future applications. Some papers report new materials; for example, a new dopant ion which shows upconversion is the U^{4+} ion [14]. Sulphide glasses might be interesting new host materials because of their low energy phonons, which prevent efficient non-radiative relaxation [15]. In other papers the upconversion mechanisms are analyzed in detail. Frequently encountered mechanisms for upconversion are excited state absorption and energy transfer. Hehlen et al. [16] showed that energy migration, even at low doping levels, is also of importance for upconversion in $Cs_3Lu_2Br_9:Er^{3+}$. Several materials show upconversion luminescence when pumped at an energy which does not correspond to a purely electronic transition from the ground state. Rather, it corresponds to a transition from a metastable excited state to a higher excited state. This mechanism is known as photon avalanche [17,18]. Auzel and Chen [17] studied the first step of this mechanism in Er^{3+} doped $LiYF_4$, which involves a very weak multiphonon sideband absorption transition.

Many models exist which describe the dynamics of energy transfer; an example is the Inokuti–Hirayama model (discussed in [1]). These models usually assume a random distribution of donors and acceptors and a continuous range of distances between donors and acceptors. Vasquez and Flint [19] found that these models do not work properly for several real crystalline systems. Models have now been tailored for specific systems. For example, very good agreement with experimental data on $Cs_2NaY_{1-x}Pr_xCl_6$ was obtained for a model which was developed to treat energy transfer in cubic lattices having the elpasolite crystal structure [19]. Furthermore, Wang and Simpkin [20] found that the upconversion dynamics in Er^{3+} doped $YAlO_3$ and YAG (yttrium aluminium garnet, $Y_3Al_5O_{12}$) are better described by a model that assumes a regular distribution of donors and acceptors.

High-resolution spectroscopy and single molecule spectroscopy

Using high-resolution spectroscopic techniques, such as fluorescence line narrowing and spectral hole burning (SHB), the homogeneous line width (i.e. the optical line width for a single ion or molecule in a solid) of a zero phonon transition of an impurity in a solid can be studied [1,21]. At low temperatures (< 4.2 K) the homogeneous line width is much smaller than the inhomogeneous width. Recently, the narrowest known homogeneous line width of an optical transition in a solid has been reported for an f–f transition of Eu^{3+} in Y_2SiO_5. The width is only 122 Hz (~ 10^{-9} cm⁻¹) measured at 1.2 K using the photon echo technique [22•]. The homogeneous line width and its temperature dependence are very sensitive probes for studying the interaction of an impurity with its surroundings [1,21]. In [23] the interaction of Eu^{3+} and Pr^{3+} impurity ions with the silicate glass host was studied

using spectral hole burning. The results showed that the optical dynamic behaviour of the two ions in the glass is not the same. For example, persistent spectal hole burning was observed for Pr^{3+} but not for Eu^{3+}.

Persistent SHB is of importance for high density optical information storage [21]. Sm^{2+} doped materials have recently been reported to exhibit persistent SHB at room temperature [24•,25]. In these materials, holes are burnt by photoionizing the Sm^{2+} ions in a two-photon process [24•]. Two-colour, two-photon ionization is also the mechanism for hole burning (at low temperatures) in $SrTiO_3:Cr^{3+}$ [26]. When the spectral hole is detected, by scanning the laser over the spectral region containing the hole and measuring the luminescence intensity, this two-photon process prevents refilling of the spectral hole.

High-resolution laser spectroscopy has been extended into the field of single molecule spectroscopy in solids (SMS) [27••]. With SMS the local environment of the molecule can be probed with an unprecedented sensitivity. In addition, SMS allows a test of theoretical models in a more convincing way, because of the absence of ensemble averaging. For example, the quantum jump between a singlet and a triplet excited state of a single terrylene molecule has been directly observed [28••]. SMS has mainly been performed on the aromatic molecules pentacene, perylene and terrylene in *p*-terphenyl crystals or in a polyethylene polymer. These systems have served as model systems for which SMS has been optimized. Recently, several new matrices have also been investigated [29].

Scanning near-field optical microscopy

A new technique, scanning near-field optical microscopy (SNOM), which has been developed since the mid-eighties, allows both microscopy and spectroscopy under very high spatial resolution [30]. The concept is related to scanning probe microscopic techniques such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM).

By scanning a very small light source in very close proximity to the surface of a sample, the $\lambda/2$ diffraction limit can be circumvented and one can use visible light to resolve details smaller than 50 nm. If the surface under investigation contains luminescent centres, only those few centres which are illuminated by the very small light source are excited. In this way a luminescent image of high resolution of the surface can be obtained. A typical design of a SNOM microscope is described in [31].

Using SNOM, single dye molecules which were dispersed on a thin polymer film could be excited and their luminescence spectrum recorded at room temperature (Fig. 2) [32••]. Excited state dynamics of single dye molecules could also be probed by time-resolved luminescence measurements using SNOM [33]. The high spatial
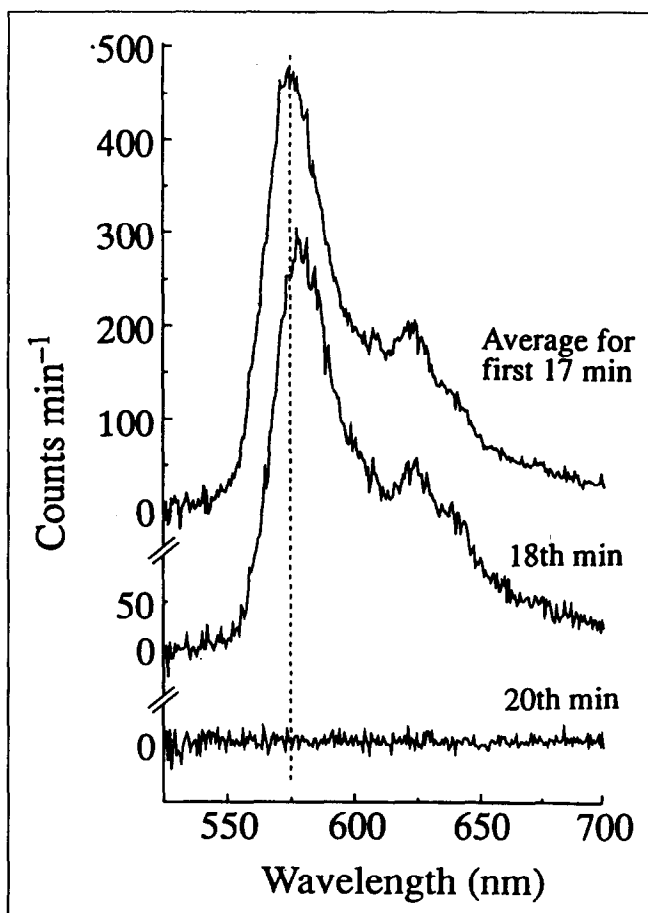
Luminescence spectra at room temperature of a single, highly photostable dil (i.e. 1,1'-dioctadecyl-3,3,3',3'-tetra-methylindocarbocyanine) dye molecule embedded in a polymethylmethacrylate (PMMA) polymer film. The spectra were measured using a scanning near-field optical microscope. Excitation was at 529 nm. The upper trace is the average of 17 spectra acquired over 17 min, during which no distinguishable spectral change occurred. During the eighteenth one-minute integration, the emission shifted about 5 nm towards the red. During the nineteenth minute the molecule was photobleached. The lowest trace (labelled twentieth minute) is the background. (Published with permission from [32••].)

resolution of the SNOM technique has been combined with a high spectral resolution in several studies [34,35••]. In [35••], a two-dimensional luminescent GaAs/AlGaAs quantum well (i.e. a thin, ≈40 Å, sheet of GaAs with a low energy band gap, sandwiched between much thicker sheets of AlGaAs with a higher energy band gap) has been investigated. The authors were able to obtain a luminescence image of the quantum well at liquid helium temperature; the luminescent centres correspond in this case to excitons localized at interface fluctuations.

The latest development in this area is the scanning interferometric near-field optical microscope, achieving a resolution of 1 nm [36•]. This is almost two orders of

magnitude better than that achieved using SNOM. The concept is related to SNOM, but the contrast mechanism is fundamentally different. In this method the dipole–dipole coupling between an electric dipole in the sample and a tip of a vibrating needle is measured.

New scintillator materials

Scintillators are inorganic materials which convert the energy of ionizing radiation into visible light. They are applied in detectors used in high energy physics experiments and in new medical imaging techniques [37,38]. The area of scintillator research is very active, because the above-mentioned applications require materials with superior properties to those of the traditional scintillators [37,38]. In particular, the new generation of scintillator materials should combine a high stopping power for ionizing radiation with high efficiency and high speed. In the traditional materials these demands were only partially met.

Crystals containing Ce^{3+} are especially interesting for application in high energy physics, because of their fast and efficient luminescence in the UV and blue spectral regions. Upon excitation with γ rays or UV light, CeF_3 crystals show luminescence from regular Ce^{3+} ions and from Ce^{3+} ions which are perturbed by nearby lattice defects such as oxygen ions. Energy transfer occurs from the former ions to the latter. Although CeF_3 is a very fast scintillator (decay time ≈ 20 ns), it has a relatively low light yield because of the low efficiency of the lattice–Ce^{3+} energy transfer upon excitation with ionizing radiation [39•]. Ce^{3+} doped oxidic materials such as $LuAlO_3$:Ce [40] and Gd_2SiO_5:Ce [41] are also promising scintillators. In [42] it is shown that Ce^{3+} ions are excited via a self-trapped exciton state of the pure oxide crystal. This means that the electrons and holes which are formed upon absorption of high energy radiation first recombine, after which the recombination energy is transferred to Ce^{3+} ions.

Luminescence of silicon

At the present time there is great interest in the possibility of using silicon in optoelectronic devices because this would allow an integration of these devices in the highly developed silicon-based microelectronics technology. However, silicon is an indirect band gap semiconductor (i.e. transitions between conduction band and valence band are forbidden) which prevents efficient luminescence. Several tricks may be applied to use silicon as a luminescent material. For example, it can be doped with rare earth ions such as Er^{3+}, or porous silicon can be used instead of bulk silicon. As this field is extremely active, it is impossible to review all the work and all the ideas which have been published recently. We will briefly discuss some selected papers.

Er^{3+} doped silicon shows photoluminescence as well as electroluminescence at about 1.55 μm due to an f–f

transition of Er^{3+} [43–45]. Er^{3+} ions can be excited via recombination of electrons and holes which are trapped at an Er-related recombination site [46]. The exact chemical environment of the optically active Er^{3+} ions is not yet firmly established. Several kinds of optically active Er^{3+} ions exist, some of which have oxygen atoms or other impurities or defects in their surroundings [47].

Although there is still no general agreement concerning the nature of the visible luminescence of porous silicon, many researchers think that it is due to quantum confinement of excitons in nanosized silicon dots and wires [48,49,50•,51•]. Very recently, the importance of Auger and Coulomb charging effects were emphasized in the explanation of the voltage tuning of the photoluminescence and the electroluminescence of porous silicon [50•,51•].

Conclusions

We have reviewed some recent papers in the field of luminescence of solids. The potential of opto-electronic applications is a major drive behind a lot of this research. New materials doped with transition metal ions or rare earth ions are or may be used as laser materials, optical amplifiers, displays or materials for optical recording. It is believed that a better understanding of the nature of the luminescent centres and the mechanisms of excitation and relaxation of these centres will eventually lead to the design of new materials. On the other hand, recent technological developments, especially in the laser area, have vastly increased the experimental possibilities of solid state optical spectroscopy, enabling for example single molecule and femtosecond spectroscopy.

Note added in proof

Recently we became aware of the publication of a book which gives an excellent introduction to the field of luminescence of solids [52].

References and recommended reading

Papers of particular interest, published within the annual period of review, have been highlighted as

• of special interest
•• of outstanding interest

1. Henderson B, Imbusch GF: *Optical Spectroscopy of Inorganic Solids.* Oxford: Clarendon Press; 1989.

2. Rose TS, Fields RA, Whitmore MH, Singel DJ: **Optical**
•   **Zeeman spectroscopy of the near-infrared lasing center in chromium:forsterite.** *J Opt Soc Am B - Opt Physics* 1994, 11:428–435.
Using optical Zeeman spectroscopy and fluorescence line narrowing techniques the authors were able to unambiguously assign the near-infrared luminescence of the laser material Cr:Mg₂SiO₄ (Cr:forsterite) to tetrahedrally coordinated Cr^{4+} ions. These ions were previously identified in this material by electron paramagnetic resonance.

3. Jia W, Liu H, Wang Y, Hömmerich U, Eilers H, Hoffman K, Yen
•   **WM: Stress effects on the fluorescence spectra of tetravalent chromium in some crystalline hosts.** *J Luminesc* 1994, 59:279–287.
Chromium-doped forsterite shows narrow line luminescence at low temperatures and broad band luminescence at room temperature; therefore, the nature of the luminescent excited state was not clear. In this paper it is

demonstrated that the luminescence of this material and other Cr^{4+} doped laser materials shows large spectral shifts under uniaxial stress. This indicates that the luminescence is due to a transition from the $^3T_2$ excited state and not from the ^1E excited state.

4. Demos SG, Alfano RR: **Subpicosecond time-resolved Raman investigation of optical phonon modes in Cr-doped forsterite.** *Phys Rev B* 1995, 52:987–996.

5. Brunold TC, Hazenkamp MF, Güdel HU: **Manganate(VI): a**
• **novel near-infrared broadband emitter.** *J Am Chem Soc* 1995, 117:5598–5599.
A new luminescent ion is reported. The luminescence spectrum of manganate(VI) extends from 7000–11 000 cm⁻¹. It shows a rich vibrational structure in several host lattices, which allows a detailed analysis of the vibronic coupling. As the luminescence of this dopant ion in several hosts persists up to room temperature, it might be interesting for future applications in tunable near-infrared lasers.

6. Riesen H, Krausz E: **Dynamic processes in the lowest-excited**
• ^{3}MLCT **states of $[M(L)_{3-x}(L')_x]^{2+}$ (L,L'=diimine; M=Ru, Os).** *Comment Inorg Chem* 1995, 18:27–63.
This paper nicely illustrates that sophisticated spectroscopic methods such as high-resolution laser spectroscopy and spectroscopy in magnetic and electric fields have now found their way to coordination chemistry. The lowest excited ^{3}MLCT state of $[Ru(bpy)_3]^{2+}$ is studied. This complex is an important photoredox system which is used in solar cells. Although the experimental work is of high quality, it should be noted that some of the conclusions are questioned by other researchers, for example those in [7].

7. Braun D, Huber P, Wudy J, Schmidt J, Yersin H: **Electron delocalisation and localisation in mixed-ligand $[Ru(LL)_n(LL')_{3-n}]^{2+}$ complexes.** *J Phys Chem* 1994, 98:8044–8049.

8. Bellafrouh K, Daul C, Güdel HU, Gilardoni F, Weber J: **Density-functional investigation of the excited state properties and the Jahn-Teller effect in $[CrX_6]^{3-}$ (X=Cl⁻, Br⁻).** *Theor Chim Acta* 1995, 91:215–224.

9. López-Moraza S, Pascual JL, Barandiarán Z: *Ab-initio* **model potential embedded-cluster study of V^{2+}-doped fluoroperovskites: effects of different hosts on the local distortion and electronic structure of $^4T_{2g}$-$^4A_{2g}$ laser levels.** *J Chem Phys* 1995, 103:2117–2125.

10. Woods AM, Sinkovits RS, Bartram RH: **Computer modelling of**
• **thermal quenching of chromium photoluminescence in fluoride elpasolites.** *J Phys Chem Solids* 1994, 55:91–94.
It is very hard to predict non-radiative relaxation properties of luminescent materials, even though this would be very welcome for the design of new materials. The authors have used *ab initio* methods to calculate non-radiative rates and quenching temperatures of Cr^{3+} doped laser materials. The agreement with experimental data is reasonable and the present results are very promising.

11. Wexler D, Zink JI, Reber C: **Spectroscopic manifestations of potential surface coupling along normal coordinates in transition metal complexes.** In *Topics in Current Chemistry*, vol 171: *Electronic and Vibronic Spectra of Transition Metal Complexes I.* Edited by Yersin H. Berlin: Springer; 1994:173–203.

12. Savoie C, Reber C, Bélanger S, Beauchamp AL: **Spectroscopic observation of coupled metal-ligand vibrational modes in the luminescence spectrum of *trans*-[ReO₂(1-methylimidazole)₄]I.** *Inorg Chem* 1995, 34:3851–3852.

13. Heine F, Heumann E, Danger T, Schweizer T, Koetke J, Huber G,
• Chai BHT: **Room temperature continuous wave upconversion Er:YLF laser at 551 nm.** In *OSA Proceedings on Advanced Solid State Lasers*, vol 20. Edited by Fan TY, Chai BHT. Washington DC: Optical Society of America; 1994:344–347.
This is the first green emitting room temperature continuous wave laser operation of an Er^{3+} doped crystal. The achievement of laser action at room temperature in a crystal is very important for future commercial applications.

14. Xu W, Dai S, Toth LM, Peterson JR: **Blue up-conversion emission from U^{4+}-ion doped into Cs_2ZrCl_6 single crystals under green light (19436 cm⁻¹) excitation.** *Chem Phys* 1995, 193:339–344.

15. Kadono K, Higuchi H, Takahashi M, Kawamoto Y, Tanaka H: **Upconversion luminescence of Ga_2S_3-based sulphide glasses containing Er^{3+} ions.** *J Non-Cryst Solids* 1995, 184:309–314.

16. Hehlen MP, Frei G, Güdel HU: **Dynamics of infrared-to-visible upconversion in $Cs_3Lu_2Br_9$:1% Er^{3+}.** *Phys Rev B* 1994, 50:16264–16273.

17. Auzel F, Chen Y: **Photon avalanche luminescence of Er^{3+} ions in $LiYF_4$ crystal.** *J Luminesc* 1995, 65:45–56.

18. Collins BC, Silversmith AJ: **Avalanche upconversion in LaF_3:Tm^{3+}.** *J Luminesc* 1994, 62:271–279.

19. Vasquez SO, Flint CD: **A shell model for cross relaxation in elpasolite crystals: application to the $^3P_0$ and $^1G_4$ states of $Cs_2NaY_{1-x}Pr_xCl_6$.** *Chem Phys Lett* 1995, 238:378–386.

20. Wang J, Simkin DJ: **Energy transfer within a regular distribution of donors and acceptors: application to the upconversion dynamics of Er^{3+}: $YAlO_3$ and Er^{3+}:YAG.** *Phys Rev B* 1995, 52:3309–3314.

21. Rebane KK: **Zero-phonon line as the foundation stone of high-resolution matrix spectroscopy, persistent spectral hole burning, single impurity molecule spectroscopy.** *Chem Phys* 1994, 189:139–148.

22. Equall RW, Sun Y, Cone RL, Macfarlane RM: **Ultraslow optical**
• **dephasing in Eu^{3+}:Y_2SiO_5.** *Phys Rev Lett* 1994, 72:2179–2182.
The homogeneous line width of the $^7F_0$–$^5D_0$ transition of Eu^{3+} in Y_2SiO_5 is only 122 Hz ($\sim 10^{-9}$ cm⁻¹) at 1.2 K. It is the smallest homogeneous line width of an optical transition in a solid reported so far. It was measured in the time domain using the photon echo technique.

23. Schmidt T, Macfarlane RM, Völker S: **Persistent and transient spectral hole burning in Pr^{3+}- and Eu^{3+}- doped silicate glasses.** *Phys Rev B* 1994, 50:15707–15718.

24. Bill H, Jaaniso R, Hagemann H, Lovy D, Monnier A, Schnieper M:
• **High-temperature spectral hole burning on samarium(II) in single crystals of the lead fluorohalide family and in thin films of calcium fluoride.** *Opt Eng* 1995, 34:2333–2338.
The authors were the first to demonstrate persistent SHB at room temperature in Sm^{2+} doped crystals, which is of importance for the use of hole burning in optical data storage. In this paper recent results on these materials are reviewed.

25. Nogami M, Abe Y, Hirao K, Cho DH: **Room temperature persistent spectral hole burning in Sm^{2+}-doped silicate glasses prepared by the sol-gel process.** *Appl Phys Lett* 1995, 66:2952–2954.

26. Silversmith AJ, Lenth W, Blazey KW, Macfarlane RM: **Photon gated spectral hole burning in $SrTiO_3$:Cr^{3+}.** *J Luminesc* 1994, 59:269–275.

27. Moerner WE: **Examining nanoenvironments in solids on the**
•• **scale of a single isolated impurity molecule.** *Science* 1994, 265:46–53.
A good overview is given of the most recent developments in the field of single molecule spectroscopy.

28. Basché T, Kummer S, Bräuchle C: **Direct observation**
•• **of quantum jumps of a single molecule.** *Nature* 1995, 373:132–134.
The quantum jump of a single terrylene molecule from the excited singlet state into the excited triplet state has been directly observed using time-dependent luminescence spectroscopy. After singlet to triplet intersystem crossing the molecule is 'dark' for a period of time corresponding to the triplet state lifetime.

29. Kozankiewicz B, Bernard J, Orrit M: **Single molecule lines and spectral holes of terrylene in different matrices.** *J Chem Phys* 1994, 101:9377–9383.

30. Heinzelmann H, Pohl DW: **Scanning near-field optical microscopy.** *Appl Phys A* 1994, 59:89–103.

31. Tarrach G, Bopp MA, Zeisel D, Meixner AJ: **Design and construction of a versatile scanning near-field optical microscope for fluorescence imaging of single molecules.** *Rev Sci Instr* 1995, 66:3569–3575.

32. Trautman JK, Macklin JJ, Brus LE, Betzig E: **Near-field**
•• **spectroscopy of single molecules at room temperature.** *Nature* 1994, 369:40–42.
The high spatial resolution of the scanning near-field optical microscopy technique (SNOM) enabled the authors to measure the first luminescence spectrum of a single dye molecule at room temperature. This opens the possibility of performing similar spectroscopic studies of biological systems at ambient conditions.

33. Xie XS, Dunn RC: **Probing single molecule dynamics.** *Science* 1994, 265:361–364.

34. Moerner WE, Plakhotnik T, Irngartinger T, Wild UP, Pohl DW, Hecht B: **Near-field optical spectroscopy of individual molecules in solids.** *Phys Rev Lett* 1994, 73:2764–2767.

35. Hess HF, Betzig E, Harris TD, Pfeiffer LN, West KW: **Near-field**
•• **spectroscopy of the quantum constituents of a luminescent system.** *Science* 1994, 264:1740–1745.

Under high spatial and spectral resolution the nature of the individual luminescent centres in a GaAs/AlGaAs quantum well is studied. The study illustrates the great possibilities of the SNOM technique, which can also be used in semiconductor physics.

36. Zenhausern F, Martin Y, Wickramasinghe HK: **Scanning**
● **interferometric apertureless microscopy: optical imaging at 10 angstroms resolution.** *Science* 1995, 269:1083–1085.
A new technique, scanning interferometric near-field optical microscopy, achieving a resolution of 1 nm, is demonstrated. The technique is related to SNOM, but relies on a different principle. In this method the sample and a small vibrating tip are illuminated by a laser. The phase difference between the beam reflected and scattered by the sample and the vibrating tip and a reference beam is measured with an interferometer. The phase difference is dependent on the dipole–dipole coupling of the vibrating tip with dipoles in the sample.

37. Blasse G: **The luminescence efficiency of scintillators for several applications: state-of-the-art.** *J Luminesc* 1994, 60–61:930–935.

38. Lempicki A, Wojtowicz AJ: **Fundamental limitations of scintillators.** *J Luminesc* 1994, 60–61:942–947.

39. Wojtowicz AJ, Balcerzyk M, Berman E, Lempicki A: **Optical**
● **spectroscopy and scintillation mechanism of $Ce_xLa_{1-x}F_3$.** *Phys Rev B* 1994, 49:14880–14895.
This is an extensive study on one of the most important new high-speed scintillator materials. It points out the importance of reducing the defect concentration in CeF_3 crystals. Several kinds of defects cause 'perturbed' Ce^{3+} ions to be formed, which are detrimental for scintillator performance. In addition, the relatively low light yield of this material is also ascribed to the low efficiency of the lattice–Ce^{3+} energy transfer.

40. Moses WW, Derenzo SE, Fyodorov A, Korzhik M, Gektin A, Minkov B, Aslanov V: **$LuAlO_3$:Ce — a high density, high speed scintillator for gamma detection.** *IEEE Trans Nucl Sci* 1995, 42:275–279.

41. Suzuki H, Tombrello TA, Melcher CL, Schweizer JS: **Energy transfer from Gd to Ce in $Gd_2(SiO_4)O$:Ce.** *J Luminesc* 1994, 60–61:963–966.

42. Korzhik MV, Trower WP: **Origin of scintillation in cerium-doped oxide crystals.** *Appl Phys Lett* 1995, 66:2327–2328.

43. Sobolev NA: **Light-emitting Si:Er structures: technology and physical properties (review).** *Semiconductors - Engl Tr* 1995, 29:595–607.

44. Polman A, Van den Hoven GN, Custer JS, Shin JH, Serna R: **Erbium in crystal silicon: optical activation, excitation and concentration limits.** *J Appl Phys* 1995, 77:1256–1262.

45. Lombardo S, Campisano SU, van den Hoven GN, Polman A: **Erbium in oxygen-doped silicon: electroluminescence.** *J Appl Phys* 1995, 77:6504–6510.

46. Shin JH, Van den Hoven GN, Polman A: **Direct experimental evidence for trap-state mediated excitation of Er^{3+} in silicon.** *Appl Phys Lett* 1995, 67:377–379.

47. Przybylinska H, Hendorfer G, Bruckner M, Palmetshofer L, Jantsch W: **On the local structure of optically active Er centers in Si.** *Appl Phys Lett* 1995, 66:490–492.

48. Schuppler S, Friedman SL, Marcus MA, Adler DL, Xie Y-H, Ross FM, Harris TD, Brown WL, Chabal YJ, Brus LE, Citrin PH: **Dimensions of luminescent oxidized and porous silicon structures.** *Phys Rev Lett* 1994, 72:2648–2651.

49. Delerue C, Lannoo M, Allen G, Martin E: **Theoretical descriptions of porous silicon.** *Thin Solid Films* 1995, 255:27–34.

50. Delerue C, Lannoo M, Allen G, Martin E, Mihalcescu I, Vial JC,
● Romestain R, Muller F, Bsiesy A: **Auger and coulomb charging effects in semiconductor nanocrystallites.** *Phys Rev Lett* 1995, 75:2228–2231.
The wavelength of the photoluminescence and the electroluminescence of porous silicon can be tuned by applying a negative voltage to the sample in an aqueous sulphate or persulphate solution. This voltage tuning can be simply and convincingly explained by the Auger effect if it is assumed that porous silicon is essentially an ensemble of small (a few nanometres) crystallites with a broad size distribution.

51. Meulenkamp EA, Peter LM, Riley DJ, Wielgosz RI: **On the**
● **mechanism of the voltage tuning of photoluminescence and electroluminescnce in porous silicon.** *J Electroanal Chem* 1995, 392:97–100.
This paper appeared at about the same time as [50●], and contains in principle the same explanation for the same observations.

52. Blasse G, Grabmaier BC: *Luminescence materials.* Berlin: Springer Verlag; 1994.