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"Giant resonances" in luminescence soft-x-ray excitation spectra of phosphors

D. B. M. Klaassen* and C. M. G. van Leuken
Philips Research Laboratories, P.O. Box 80 000, 5600 JA Eindhoven, The Netherlands

K. M. H. Maessen
Department of Technical Physics, Utrecht State University, Princetonplein 5, 3508 TA Utrecht, The Netherlands

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Effects of the $4d \rightarrow 4f$ "giant resonances" of rare-earth constituents in phosphor host lattices were observed for the first time by means of luminescence excitation spectroscopy. Sintered powder samples of rare-earth (La,Gd) oxysulfides activated with terbium or europium were excited using monochromatic synchrotron radiation with photon energies between 100 and 200 eV. Whereas the total-photoelectron-yield spectra showed an enhancement of photoemission at the excitation energies corresponding to the $4d \rightarrow 4f$ giant resonances of lanthanum or gadolinium, a drop in luminescence intensity was observed at these energies. This apparent discrepancy with expectations from optically detected extended x-ray-absorption fine-structure measurements is discussed.

I. INTRODUCTION

Applications of luminescent materials (phosphors) can be distinguished by their methods of excitation: uv radiation, x rays, or high-energy electrons. Whereas in the latter methods the luminescent centers (activators) are excited by thermalized electron-hole pairs, in the first method the uv radiation is often directly absorbed by the activators. To understand the efficiencies of these excitation methods and the processes of energy transfer, it is of special interest to study the intermediate range of excitation energies. Vacuum-uv excitation spectra yield information about the position and width of deep-lying levels (Ref. 1 and references cited therein). Moreover, extension of the excitation energies to the soft-x-ray region opens the possibility of photoelectron spectroscopy. With this technique the energy levels of the constituent atoms can be determined relative to the bands of the lattice (Refs. 2 and 3).

Here we report on measurements of luminescence excitation spectra of phosphors in the energy region between 100 and 200 eV. In the following two sections the experimental setup at the 2.5-GeV synchrotron of the University of Bonn (Federal Republic of Germany) and preparation of the phosphor samples are described. In later sections the excitation spectra are presented and discussed, together with the simultaneously obtained total-photoelectron-yield spectra.

II. EXPERIMENTAL

Experiments were performed at the 2.5-GeV synchrotron of the University of Bonn. The radiation was monochromatized by the MAXIMOC monochromator (Refs. 4–7) equipped with a 1200-groove/mm grating. A rotatable exit mirror was mounted to direct the exciting radiation coming out of the MAXIMOC into the sample chamber. The integral visible terbium or europium luminescence intensity was detected with a photomultiplier, while the photoelectrons were detected with a channeltron (both from the front surface of the sample). The signals of both photomultiplier and channeltron were processed using pulse-counting techniques, and stored on floppy disks of a microcomputer.

At each excitation wavelength the focusing entrance mirror and the grating were positioned according to the procedures described in Refs. 6 and 7. The entrance and exit mirrors were rotated to get optimum zero-order signal from the grating (detected with a separate photodiode) and optimum luminescence signal, respectively. All settings were computer controlled, resulting in fully automated scanning of the MAXIMOC monochromator and measurement of excitation spectra.

The overall performance, calibration, and resolution of the excitation setup were checked by measuring the $L_{2,3}$ absorption edge of a thin aluminum foil using a channeltron as detector. The resolution was measured to be about 0.2 eV at an obtained position of the edge of 72.9 eV. According to Püster (Ref. 7) the resolution varies from 0.4 eV at 100 eV to 1.5 eV at 200 eV. Considering the different grating and the large slit widths used in the monochromator (over 100 μm to get maximum signal), the measured resolution is well within the expectations.

III. PHOSPHOR SAMPLES

Lanthanum and gadolinium oxysulfides activated with terbium or europium ($La_{1.988}Tb_{0.012}O_2S$, $La_{1.98}Eu_{0.02}O_2S$, $Gd_{1.998}Tb_{0.012}O_2S$, and $Gd_{1.98}Eu_{0.02}O_2S$) were prepared by the usual ceramic techniques (Ref. 8). These phosphors showed the characteristic green terbium (545 nm) or europium (612 nm) emission and had quantum efficiencies (under excitation at 254 nm) of about 50% (Tb) and 90% (Eu). The powders were processed to tablets using a hydraulic press. The tablets (about 15 mm in diameter) were sintered at 1500 K in nitrogen atmosphere. Pieces of about 10×4 mm^2 and 2 mm thick, cut from these tablets, were mounted in the sample holder.

IV. RESULTS

Fluctuations in the synchrotron-radiation intensity were monitored by means of the reference photodiodes (see Fig. 4 of Ref. 6). The signals from the photomultiplier and channeltron were corrected for these fluctuations and for the background. Spectra measured in repetitive scans on the same sample were plotted with a logarithmic intensity scale and shifted vertically to get coincidence. The luminescence excitation spectra of the four samples are given in Fig. 1. Except for the structure around 120 eV for the lanthanum oxysulfides and around 150 eV for the gadolium oxysulfides, the luminescence intensity shows an exponential dependence on the excitation energy. This exponential behavior is caused mainly by the fact that the intensity of the exciting radiation is strongly dependent on the energy (Ref. 7). The small difference in this overall dependence on the excitation energy between the luminescence intensities of the lanthanum oxysulfides and gadolinium oxysulfides is discussed in Sec. V. The luminescence excitation spectra, corrected for the exponential dependence, are given in Fig. 2. Clear dips are observed at about 120 eV for the lanthanum oxysulfides and at about 150 eV for the gadolinium oxysulfides. The widths are on the order of 30 and 10 eV, respectively. The relative depth of the dips varies from 25 to 50 % (see Fig. 2).

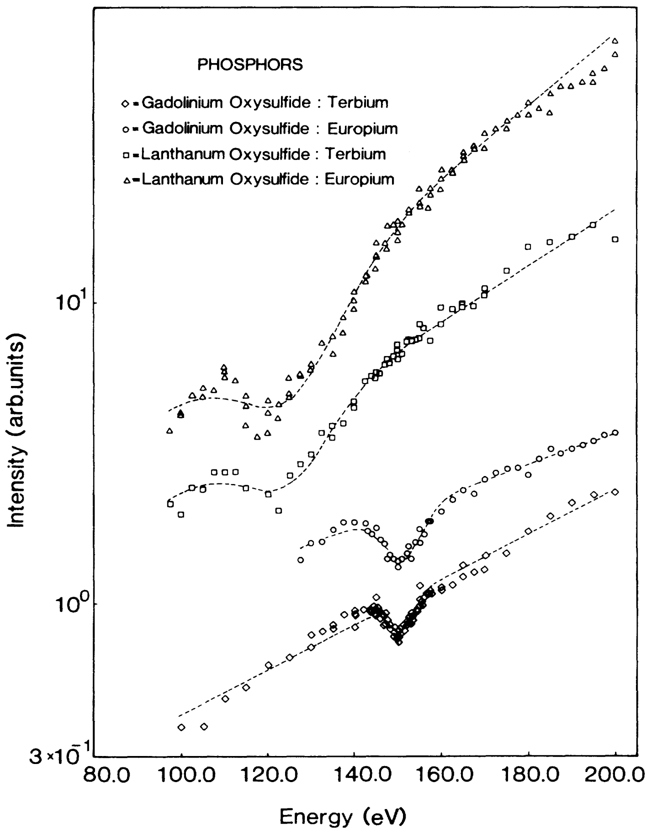

FIG. 1. Survey of luminescence excitation spectra of the rare-earth (La,Gd) oxysulfides activated with terbium or europium. Different scans for the same sample are not indicated. The spectra of different samples are shifted with respect to each other. Dashed lines are for visual aid only.

No effects of the giant resonances of the activators terbium or europium were found, presumably due to the low activator concentration.

The total-photoelectron-yield spectra were measured with a channeltron. Since the channeltron used also had considerable detection efficiency in the soft-x-ray region, the channeltron signal was examined by shielding off the channeltron with a small-mesh wire netting at −2 kV. The signal decreased 2 orders of magnitude, indicating that the contribution of synchrotron radiation to the signal could be neglected. No attempts were made to measure the dependence of the channeltron signal on the voltage applied to the mesh, because interpretation might be quite difficult (Ref. 9). The total-photoelectron-yield spectra obtained, corrected for an overall exponential energy dependence in the same way as the luminescence excitation spectra, are shown in Fig. 3. It should be mentioned that, once mounted in the sample chamber, the samples were not subjected to any special cleaning (e.g., Ar sputtering). Because of the small escape depth of the photoelectrons (1–3 nm), contamination of the samples is expected to affect the electron-yield spectra much more than the luminescence excitation spectra. Moreover, contamination of the samples may not only influence the overall electron yield, but may also have some influence on the shape of the spectra (Ref. 10). In spite of this, clear peaks in the total-photoelectron-yield spectra are observed (see Fig. 3) at, within the experimental uncertainty, the same excitation energies as the dips in the luminescence excitation spectra; the widths are roughly half of these.

V. DISCUSSION

The positions of the structure observed in the luminescence excitation spectra, combined with the fact that at the same positions peaks are also observed in the total-photoelectron-yield spectra, points to the $4d \rightarrow 4f$ giant resonance in the lanthanum or gadolinium atom, respectively, as being the responsible mechanism. These $4d \rightarrow 4f$ giant resonances at 120 eV for lanthanum and 150 eV for gadolinium are well known and have been observed by different methods: by photoabsorption measurements on thin films (Refs. 11 and 12) and vapors (Refs. 13–15), by photoelectron spectroscopic measurements (Refs. 3 and 16–18), and in Auger spectra (Refs. 16 and 19). The correspondence between x-ray absorption and uv luminescence excitation spectra was observed for the first time by Bianconi *et al.* (Ref. 20) in the region of 4000 eV. From this correspondence the method of measuring extended x-ray-absorption fine-structure (EXAFS) spectra via optical luminescence was developed (Refs. 21–23). Here we report the first effects of $4d \rightarrow 4f$ giant resonances observed in luminescence excitation spectra of phosphors.

From the available interpretation of optically detected EXAFS (Refs. 21–23), a peak in the luminescence excitation spectrum is expected at the position of a giant resonance in the absorption. In analogy to the interpretation of x-ray fluorescence detection of EXAFS (Ref. 24), only absorption and scattering of both exciting x rays and generated radiation are considered in the interpretation of detection of EXAFS by optical (uv–visible) luminescence (Refs. 21–23). Diffusion of the “intermediate” (Ref. 25) electron-hole (*e*-*h*) pairs to the surface, followed by nonradiative recombination, is neglected. This can be justified as long as these losses are constant when an edge in the absorption coefficient of the exciting x rays is traversed. This condition is fulfilled if the penetration depth of the exciting x rays is much larger than (i) the diffusion length of the *e*-*h* pairs for monocrystalline samples (that are optically thick to x rays), and (ii) the grain size for powder samples.

In the energy range used in the present study (100–200 eV) the absorption coefficient of the exciting x rays is on the order of 10^5 cm^{-1}, resulting in a penetration depth that is an order of magnitude smaller than the grain size. Further, the effective absorption coefficient of the optical luminescence is only about 10^2 cm^{-1} (Ref. 26). Therefore, taking the internal quantum yield constant for the moment, in the interpretation of the effect of $4d \rightarrow 4f$ giant resonances on luminescence excitation only surface recombination of *e*-*h* pairs has to be considered. This can be done by using Eq. (6) of Wittry and Kyser (Ref. 27) adapted for the presence of a “dead layer.” This formula describes the ratio of apparent efficiency and bulk efficiency in terms of the absorption coefficient of the exciting radiation, the diffusion length L of the *e*-*h* pairs, the reduced (dimensionless) surface recombination velocity S, and the thickness d of the dead layer. The absorption coefficients of the exciting x rays were calculated as a function of energy for gadolinium and lanthanum oxysulfide from the data of Henke *et al.* (Ref. 28). The parameters L, S, and d were determined for gadolinium oxysulfide activated with terbium by fitting the efficiency under cathode-ray excitation of the terbium luminescence as a function of the accelerating voltage to Eq. (13) of Wittry and Kyser (Ref. 27). As shown in Fig. 4, a good agreement between theory and experiment is obtained. Combining the x-ray absorption coefficients with the parameters obtained in the fit, we calculated the effect of enhanced surface recombination on our luminescence ex-

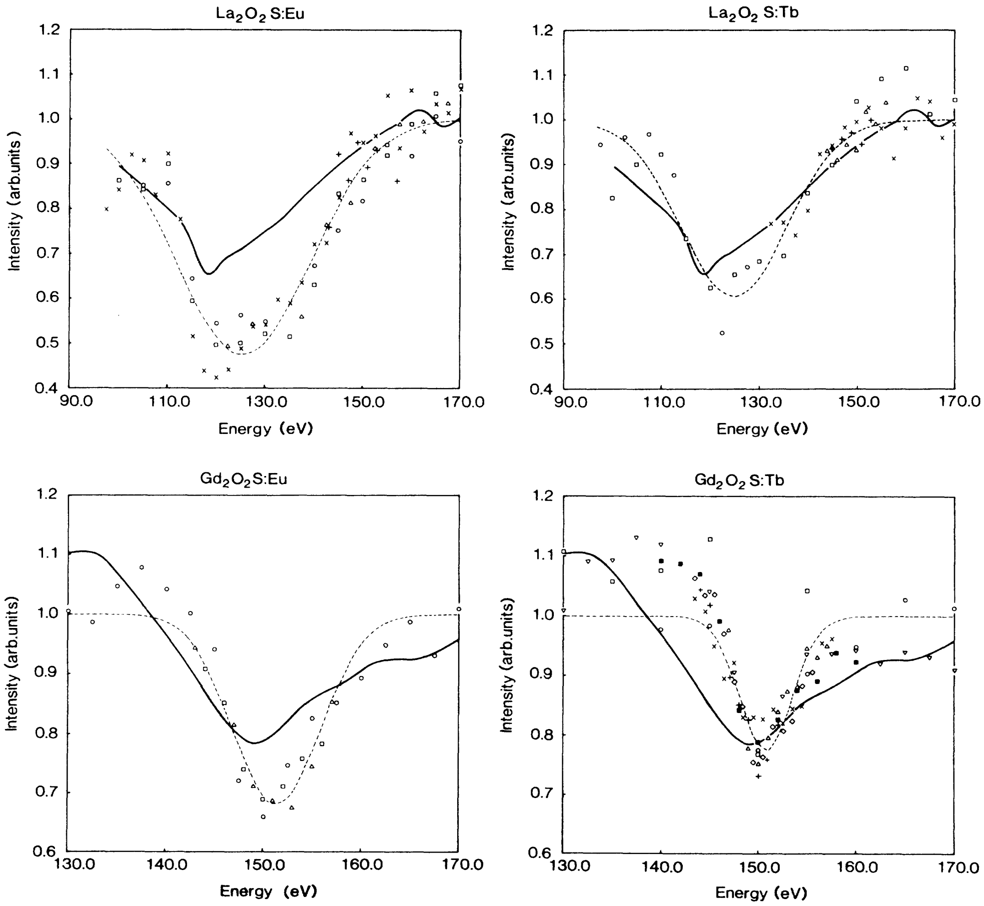

FIG. 2. Luminescence excitation spectra corrected for exponential energy dependence (see text). Different scans are indicated with different symbols. Dashed lines (for visual aid only) are the corrected lines from Fig. 1. Solid lines result from calculations (see text).

citation spectra. These theoretical spectra, given in Fig. 2, show clear dips at the positions of the giant resonances.

Once established that high absorption coefficients for the exciting x rays lead to negative edges in the optical luminescence excitation spectra, it is interesting to point to an apparent discrepancy between published experiments that can now be clarified. Bianconi *et al.* (Ref. 20) found a negative edge in the optical luminescence excitation spectrum of monocrystalline CaF_2 at the K edge of Ca, whereas Goulon *et al.* (Ref. 23) found a positive edge for a powdered sample. As the absorption coefficient of CaF_2 at the K edge is on the order of 10^3 cm^{-1}, the positive edge for the powdered sample can be explained according to the interpretation for optically detected EXAFS (Refs. 22 and 23). For the monocrystalline sample the absorption of the uv luminescence, which would lead to a positive edge, may be neglected. In order to estimate the effects of surface recombination of *e-h* pairs mentioned above, we determined L, S, and d for a powder sample of CaF_2, activated with 1 mole % terbium in order to get visible luminescence (see Fig. 4). Using the values obtained for L, S, and d, we calculated a negative edge of 1% for the uv luminescence excitation spectrum, whereas the observed value is 4% (Ref. 20). It should be noted, however, that our value is a lower limit because in our calcium fluoride sample the diffusion length of *e-h* pairs may be reduced by the doping with terbium.

The accuracy of the present measurements does not allow for a more quantitative interpretation than given in Fig. 2. The difference in width of the resonances observed between lanthanum and gadolinium is roughly in agreement with the calculations. It should be noted, however, that the data used to calculate the absorption coefficients (Ref. 28) failed to reproduce the exact shape of the giant resonances observed for atomic gadolinium (Ref. 15) and lanthanum (Ref. 13). Using the same formula as for the theoretical lines in Fig. 2, it can be shown that the width of the resonances in luminescence excitation spectra are larger than those in the total-photoelectron-yield spectra, which is in agreement with our measurements (Figs. 2 and 3).

The "amplitude" of the giant resonances observed in the luminescence excitation spectra will be affected by a

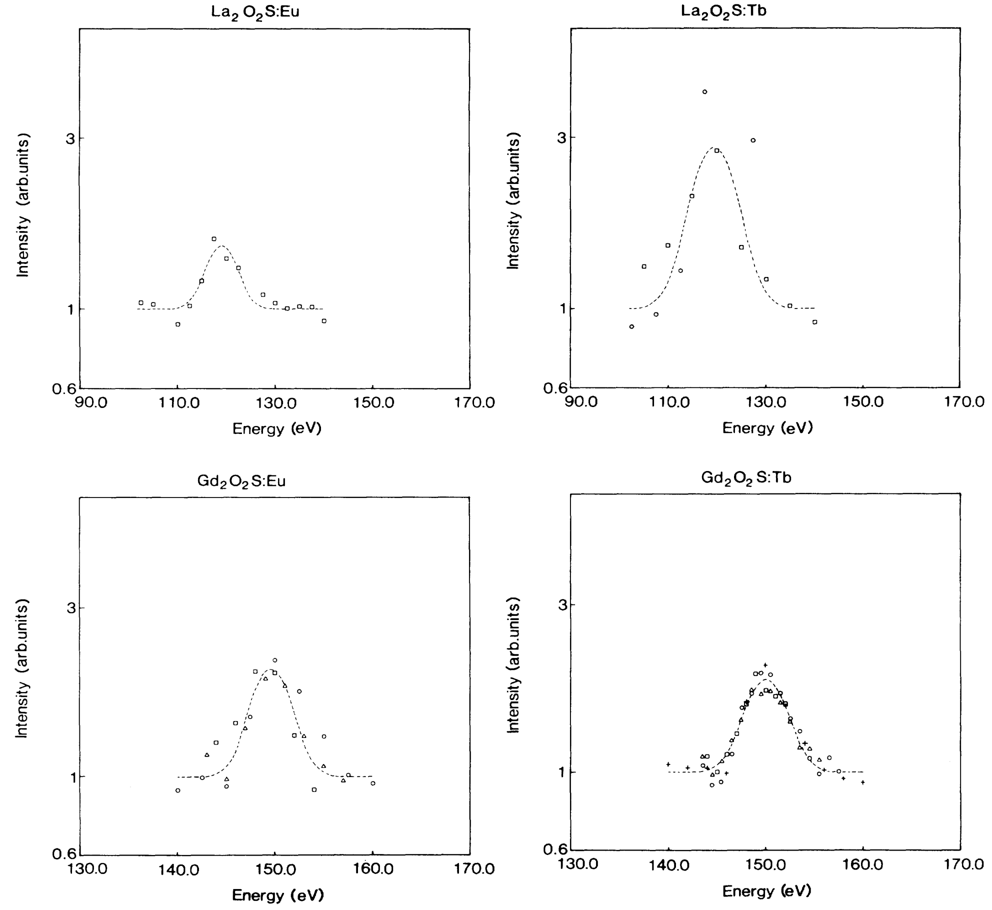

FIG. 3. Total-electron-yield spectra corrected for exponential energy dependence (see text). Different scans are indicated with different symbols. Dashed lines are for visual aid only.

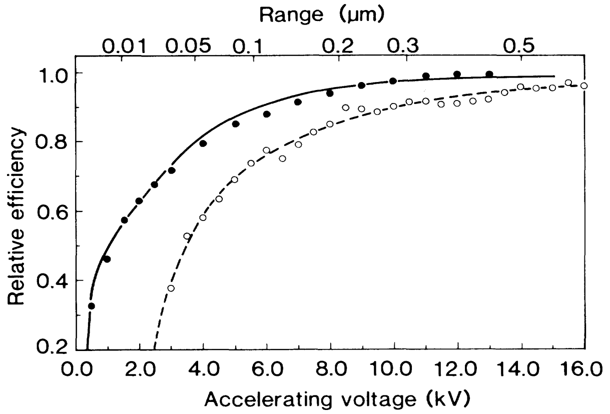

FIG. 4. Efficiency under cathode-ray excitation (measured from the bombarded side) as a function of the accelerating voltage for powder samples of gadolinium oxysulfide and calcium fluoride, both activated with terbium. The range of the primary electrons in gadolinium oxysulfide is also indicated. Solid circles represent the measurements for gadolinium oxysulfide; the solid curve was calculated from Eq. (13) of Ref. 27 with the parameters $L = 21$ nm, $S = 1.1$, and $d = 0.47$ nm. Open circles represent the measurements for calcium fluoride; the dashed curve was calculated from Eq. (13) of Ref. 27 with the parameters $L = 152$ nm, $S = 0.39$, and $d = 34$ nm. It should be mentioned that we used $u_0 = 0.322$ and $\Delta u = 0.336$ in the excitation function of Ref. 27 in order to get optimum agreement with the more realistic depth-dose curve of Everhart and Hoff (Ref. 29).

change in internal quantum yield at the giant resonance. Outside the giant resonance, photons are absorbed in the valence band or in the higher core levels of constituent atoms of the phosphor, resulting in a "hot" *e-h* pair. This "hot" *e-h* pair produces, in a cascade process, several "thermal" *e-h* pairs (Refs. 30 and 31), which finally excite the activators. At the energy of a $4d \rightarrow 4f$ giant resonance, however, the photons are preferentially absorbed in the $4d$ level. Since the resulting $4f^{n+1}$ configuration decays mainly via channels producing only one "cold" (or "thermal") *e-h* pair (Refs. 3 and 17), at the resonant energy fewer activators are excited. This change in the energy distribution of generated (primary) *e-h* pairs also follows from the enhanced x-ray fluorescence of gadolinium or lanthanum (Ref. 32) at the giant resonance, as argued by Bianconi *et al.* (Ref. 20). From Fig. 2 one might get the impression that at the giant resonance the quantum yield is indeed lower for some of the investigated phosphors. However, from the present measurements the relative importance of these hot and cold decay channels for the luminescence excitation process cannot be deduced.

The dips observed in the luminescence excitation spectra are the first reported effects of $4d \rightarrow 4f$ giant resonances on the excitation of phosphors. Cascade generation of *e-h* pairs, which finally excite the activators, forms the basis of the explanation of the observed effects. Further luminescence excitation measurements combined with energy-resolved photoelectron spectroscopy will certainly yield valuable information about the processes that determine the efficiency of the luminescence excitation.

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[*] Author to whom correspondence should be directed.

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