X-ray luminescence of phosphor crystals excited by X-ray standing waves

1992 J. Phys.: Condens. Matter 4 961

(http://iopscience.iop.org/0953-8984/4/4/006)

J. Phys.: Condens. Matter 4 (1992) 961–964. Printed in the UK

X-ray luminescence of phosphor crystals excited by x-ray standing waves

S I Zheludeva, M V Kovalchuk, I V Bashelhanov and L V Samoilova
Institute of Crystallography, Academy of Sciences of the USSR, 117333 Leninsky Prospekt 59, Moscow, USSR

Received 18 July 1991

Abstract. The formation of XRSW under Bragg diffraction conditions was demonstrated using such non-traditional secondary radiation as x-ray photoluminescence.

An x-ray standing wave (XRSW) field is formed as a result of interference between incident and diffracted waves Bragg diffracted in a perfect crystal. By measuring the angular dependence of the secondary radiation excited by XRSW, we can get structural information about the crystal surface and we can determine the position of impurity of atoms in the crystal and chemisorbed atoms on the surface (Batterman 1964, Kovalchuk and Kohn 1986). The types of secondary radiation used in XRSW are fluorescent radiation, photoemission, internal photoeffect, thermal diffuse and Compton scattering.

Each of these types of secondary radiation allows us not only to obtain structural information, but also to characterize the physical processes of its origin. The external photoeffect and fluorescent radiation reflect the specific features of inner-shell electrons; Compton scattering yields information about outer-shell electrons; and the internal photoeffect in semiconductors is connected with electrokinetic parameters, which are determined by the zone crystal structure.

Until now, interesting secondary processes such as x-ray luminescence of phosphor crystals (determined by optical properties and reflecting zone crystal structure) were not investigated in XRSW methods, except by Brummer and Stephanik (1976).

Phosphor crystals are usually insulators with a small amount of impurities (or activators), the ions of these activators being the centres of luminescence and mainly defining the excited luminescence spectrum. Luminescence has been investigated intensively by synchrotron radiation (SR) as wide-zone (5–20 eV) crystals are widely used as luminophors and can be excited by ultraviolet regions of the SR spectrum. Moreover, for an understanding of the mechanism of luminescence, higher energy levels of excitation (including the x-ray spectral range when electrons of inner shells are excited) seems to be of particular interest (Ternov and Milhailin 1986).

Crystals under investigation using the XRSW method should be of high structural perfection. Unfortunately, most x-ray luminophors working in the visible spectral range are obtainable only as powders or thin amorphous films. Nevertheless, there are single crystals of CaF_2 of sufficient quality and garnet crystals doped with rare-earth impurities which are good luminophors and in which the XRSW has been demonstrated

0953-8984/92/040961+04$04.50

with the help of fluorescence and photoemission (Lagomarsino *et al* 1984, Zheludeva *et al* 1988).

The aim of this work is to reveal the presence of XRSW *in phosphor crystals* under Bragg diffraction conditions using x-ray luminescence and thus increase the number of secondary processes traditionally used in XRSW experiments.

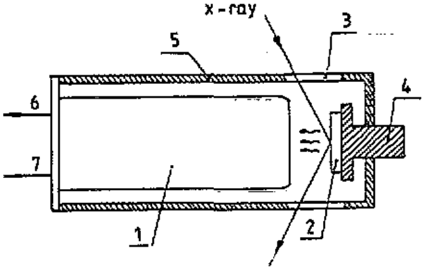

Figure 1. Special set-up for luminescence registration: 1—channeltron; 2—sample; 3—light protecting screen; 4—sample holder; 5—metal box; 6—energy supply; 7—signal to a multichannel analyser.

For x-ray luminescence measurements a special setup has been designed and constructed (figure 1). This was attached to the goniometer of a double-crystal spectrometer. A photoelectron multiplier connected with a multichannel analyser was used for x-ray luminescence registration. The experiment was performed with an x-ray tube, Mo Kα = 17.4 keV radiation, and a Si(III) crystal and a $Y_3Al_5O_{12}$(III) crystal were used as monochromators for the CaF_2 and garnet structures, respectively. Angular dependences of x-ray reflection and luminescence yield were registered during a slow scan with the help of a stepper motor. The number of photon counts was about 10^3–10^4 at each data point.

Figure 2 represents experimental results for CaF_2. The angular dependence of the luminescence looks like a reverse reflection curve showing the influence of the so-called extinction effect, well known in XRSW for fluorescence from the bulk and internal photoeffect (Kovalchuk and Kohn 1986, Zheludeva and Kovalchuk 1985). The CaF_2 crystal is transparent to the emitted light, i.e. the yield depth of the luminescence is practically equal to the photoelectric absorption depth (up to tens of microns). This defines a rather high level of luminescent signal outside the Bragg range. Under Bragg diffraction conditions, according to the dynamical theory, SW penetrates the crystal to the extinction depth, L_{ext}, only. This is about several microns and leads to a drastic decrease in the luminescence yield. Consequently, the angular dependence of the emitted luminescence is a reverse reflection curve and the phase-sensitive part (reflecting the movement of SW nodes and antinodes) is absolutely destroyed. We have the same situation for bulk garnet crystals with Nd atoms as centres of luminescence.

The problem was to find a way to decrease the yield depth and to reveal the luminescence modulated by XRSW, otherwise structure investigations using this secondary process cannot be carried out. One way is to use crystal layers of appropriate thickness, for example, epitaxial films of garnet, which are the basis of magnetostatic waves planar devices.

We have investigated a heterostructure comprising $Gd_3Ga_5O_{12}$ crystal with an

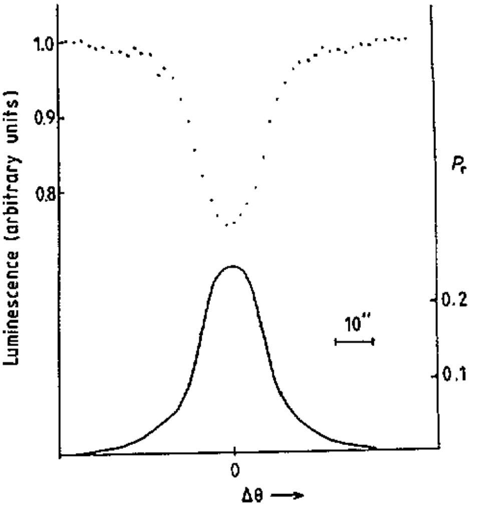

Figure 2. Experimental reflection curve and the luminescence yield for CaF_2.

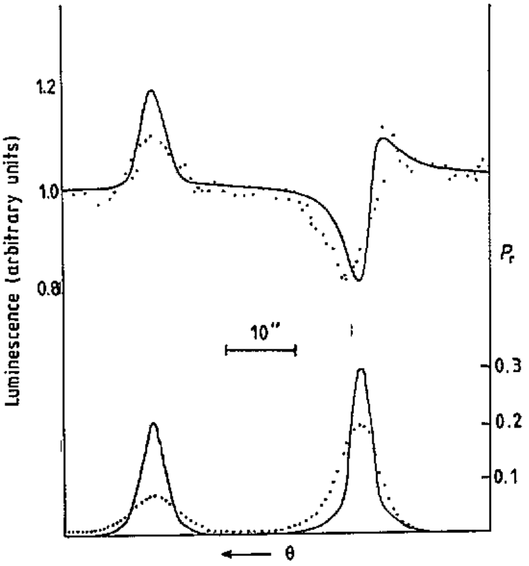

Figure 3. Experimental and calculated reflection curves and x-ray luminescence yield for the $Y_3Fe_5O_{12}/Gd_3Ga_5O_{12}$ heterostructure—(444) reflection.

epitaxial film of $Y_3Fe_5O_{12}$ on the top which was 4 μm thick and doped with rare-earth elements, so that luminescence was excited in the film only.

The experimental and calculated curves are presented in figure 3 (dotted and solid lines, respectively). The calculation procedure was based on the x-ray dynamic diffraction theory for the bicrystal model (Zheludeva *et al* 1988), taking into account that all the crystal atoms participate in luminescence in proportion to the probability of their interaction with the incident radiation. The discrepancy between theory and experiment is connected with crystal imperfections, such as mosaicity, which have not been taken into consideration since the aim was to demonstrate the possibilities of XRSW luminescence qualitatively.

The film is thick enough to form XRSW (L_{ext} is 2.6 μm). As the fluorescence yield depth is limited by film thickness and is comparable with L_{ext}, the angular dependence of fluorescence reflects the movement of SW nodes and antinodes towards the lattice planes (see the right-hand part of the upper curve). The maximum corresponds to the situation when an antinode coincides with the lattice plane leading to the enhancement of photoelectron interaction of x-rays with the crystal and hence the increase of fluorescence yield; the minimum corresponds to the node crossing the lattice plane.

The angular dependence of luminescence near Bragg diffraction from the substrate (left-hand part of figure 3) looks like the curve from the amorphous layer. In that case an XRSW field is formed in the substrate and its period is determined by the substrate d-spacing, which differs from that of the film. As luminescence is generated only in the film and there is no correlation between the position of atomic planes of the film and XRSW formed in the substrate and extending into the film the film seems to be disordered from the SW point of view.

The experiment discussed above showed that XRSW can be detected with the help of luminescence, modulating its angular dependence in the Bragg diffraction region. This secondary radiation as well as other radiations generated by photoelectron interaction of x-rays with matter may be used to characterize the structure of phosphor crystal surface layers and thin films.

The specific feature of luminescence is that, like the internal photoeffect (Zheludeva and Kovalchuk 1985), it is an 'integral' process and does not reflect the excitation of definite atoms, like x-ray fluorescence for example.

As it has been mentioned, investigation of such secondary radiations is interesting from the point of finding correlations between the structure and the physical properties of crystal.

Thus internal photoeffect allows us to relate electrical characteristics, such as the value of space charge area in a semiconductor barrier and the diffusion length of minority carriers, to structure parameters of the crystal matrix (Zheludeva and Kovalchuk 1985).

Further XRSW luminescence studies, extended by spectral composition investigations of excited luminescence and SR application, may elucidate the correlation between optical characteristics and structure parameters of phosphors.

References

Batterman B 1964 *Phys. Rev.* **133** A759

Brummer O and Stephanik H 1976 *Dynamische Interferenztheorie* (Leipzig: Akademische Verlagsgesselschaft) (in German)

Kovalchuk M and Kohn V 1986 *Usp. Fiz. Nauk.* **149** 69

Lagomarsino S, Scarinci F and Tucclarone A 1984 *Phys. Rev.* B **29** 4859

Ternov I and Mihailin V 1986 *Synchrotron Radiation* (Moscow: Atomizdat) (in Russian)

Zheludeva S and Kovalchuk M 1985 *Sov. Phys.-Semicond.* **19** 982

Zheludeva S, Kovalchuk M and Kohn V 1985 *J. Phys. C: Solid State Phys.* **18** 2287

Zheludeva S, Zakharov B, Kovalchuk M, Kohn V, Sozontov E and Sosphenov A 1988 *Crystallography* **33** 1352