High-energy anti-Stokes emission from zinc sulfide single crystals

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Some radiation emitted during the luminescence of ZnS crystals at room temperature can penetrate through aluminum foil and black paper. A dislocation mechanism is offered to explain the basic features of this phenomenon.

Photographic film wrapped in foil (10 μm thick) or black paper (in which there were no holes, according to examination under a microscope) was placed beside a crystal of ZnS–Cu, ZnS–Cl, or ZnS–Cu, Cl, with dimensions ranging from $1\times0.5\times0.5$ to $5\times3\times1$ mm, as it luminesced under the influence of UV light. A few hours later the film was developed, and a blackening was observed. This blackening was usually extremely nonuniform over the area of the film, and furthermore it varied markedly from one experiment to another. Electrical excitation of the luminescence yielded the same results. When a piece of a material equivalent to Teflon was excited by UV light, a blackening did not result. Furthermore, blackening did not result in the case of a ZnS–Cu crystal which was not excited or when the UV light beam itself was turned directly on the wrapped film.

The film was next placed in a cassette with windows consisting of one or several layers of aluminum foil. The film was pressed against the diaphragm by a piston which was screwed into the cassette from the side opposite the window. In some experiments, a polystyrene-based scintillator was placed between the piston and the film. The radiation which was transmitted through the window struck the film surface masked by the diaphragm. The part of the radiation which passed through the film was absorbed in the scintillator and produced a visible emission which illuminated the film from the other side.

Figure 1 shows a photograph from one of the cases which was "successful" in terms of uniformity of the blackening. We can see the doubled contour of the diaphragm. The inner contour, which corresponds to the actual dimensions of the diaphragm, was caused by the absorption of radiation in the film, while the outer contour was caused by emission from the scintillator which arose in a layer of a certain thickness and which was emitted from this layer within the angle of total internal reflection. From the distance between these contours we estimated the thickness of the emitting layer of the scintillator, i.e., the depth to which the photons penetrated into it. We then used this thickness to calculate the average energy of the photons, $h\nu_{em}$. We found $h\nu_{em}\approx1$ keV (with a possible error of a factor of two in either direction). Another way to estimate $h\nu_{em}$ was to cover part of the window with some additional layers of foil and to compare the blackening which resulted from the radiation which passed through the aluminum layers of different thicknesses. Despite the nonuniformity of

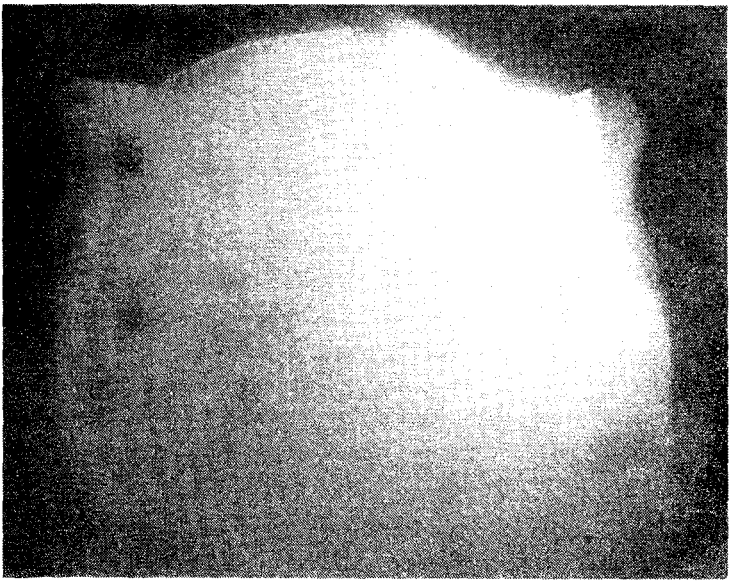

FIG. 1.

the incident flux, we were able to establish that 10 μm of aluminum attenuates the flux by a few percent and corresponds to approximately the same values of $h\nu_{em}$. Measurements with a DRGZ-02 scintillation dosimeter showed that the radiation rises some 10 s after the excitation is begun and then decreases by a factor of several units. The intensity of this radiation fluctuates markedly, having an average value of 2–6 nR/s, but on occasion it briefly increases by a factor of 10. After the excitation is turned off, the radiation also goes through a maximum and then decays. Its average power is on the order of 10^{-12} W. This figure corresponds to thousands of photons with $h\nu = 1$ keV per second. The energy yield is $10^{-10\pm1}$.

The presence of an afterglow definitely shows that this radiation is luminescence. Since it is excited by photons with $h\nu < 4$ eV, the radiation could arise only as a result of a collective effect, in which the energies of many photons are added together. We would like to suggest that the radiation is generated by plasmons, which appear during the nearly simultaneous recombination of a large number of electrons and holes which have been trapped by edge dislocations of opposite signs during the luminescence. Dislocations with unsaturated chemical bonds of one type are capable of trapping charge carriers of only one sign. During recombination luminescence, these dislocations become charged, and they are attracted to dislocations of the other sign so strongly that the dislocations begin to move toward each other. In the process they bend toward each other, since they remain pinned at the positions of impurity atoms. The charges trapped by such dislocations are pulled toward each other by electrostatic forces in the region where the dislocations come closest together, with the result that the attraction is intensified even further. Finally, they come so close together at some point that an intense tunneling of electrons begins to occur from one dislocation to the

other. Nearly all of the energy stored in the dislocations is released in a brief time, at essentially a single point. The effect is to create high-energy plasmons which are capable of creating photons with $h\nu_{em} \approx 1$ keV. After recombination, elastic forces return the dislocations to their original positions, and the process repeats itself. As a result, the crystal may emit high-energy photons for tens of hours.

This mechanism explains the basic features of the radiation:

1. Fluctuations in the intensity during continuous excitation. As we know, the motion of dislocations can excite acoustic phonons and at the same time itself be stimulated by these phonons. Accordingly, the pair of dislocations which is "the first to operate" helps certain other dislocations start moving; the latter help yet others start moving; and so forth. The result is a brief flash, after which a certain amount of time is required for new amounts of charge to build up on the dislocations.

2. Nonmonotonic behavior of the buildup. After recombination, some of the dislocations do not manage to return to their original position, since charge has again built up on them and forces them to begin to move toward each other. However, this charge will be smaller than the original charge, since the motion of the dislocations toward each other began at a smaller separation. For this reason, the energy released in the course of the recombination will also be smaller, and it may not be sufficient to excite a high-energy plasmon. The effect would be to reduce the effective number of dislocation pairs which are acting and thus to reduce the emission intensity.

3. Nonmonotonic behavior of the afterglow. The afterglow itself arises because nonequilibrium charge carriers also accumulate on point defects and can move from these defects to dislocations after the excitation is turned off. The charge-carrier density falls off gradually; the dislocations may move further and further apart; and an increasingly greater charge can therefore build up on them. The result will be to increase the effective number of operating dislocation pairs and thus the radiation intensity. When the number of charges stored at the point defects becomes sufficiently depleted, the radiation will nevertheless decay.

4. Directionality. The directionality of some of the radiation may be associated with an orientation along the (110) direction of dislocations which emerge at the surface facing the film.

5. The magnitude of the efficiency. An estimate shows that the mutual repulsion of the charges on a rectilinear dislocation would keep these charges from moving closer to each other than 50–80 Å. At this charge density the electrostatic interaction between interactions would be noticeable only if the dislocations lay within 500 Å of each other. If the density of dislocations were 10^6 cm^{-2}, such pairs would constitute only 10^{-4} of the total number of dislocations, but they alone would generate high-energy photons. The concentration of unsaturated bonds in them would be on the order of 10^9 cm^{-3}. Accordingly, at a concentration on the order of 10^{18} cm^{-3} for the trapping centers, the latter would collect something on the order of 10^{-9} of the total number of electrons and holes which are generated in the course of the excitation, but not all of their energy would be converted into the energy of the photons that are emitted. The efficiency would thus be $\leqslant 10^{-9}$, in agreement with experiment.

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