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CATHODOLUMINESCENCE AT DISLOCATIONS IN DIVALENT OXIDES

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Observations of cathodoluminescence of dislocations are described, both in SEM and STEM. It appears that fresh dislocations cause luminescence in a very wide range of insulators, although the models necessary to describe details of the phenomenon need further development.

1. Experimental techniques

An array of hardness indents was put into the cleaved 100 face of a MgO single crystal. These were observed in a scanning electron microscope modified for use in the cathodoluminescence mode. Total cathodoluminescence detection is by means of a quartz lens, placed close to the specimen, focussing light onto an EMI 9558 photomultiplier. For spectral analysis the photomultiplier is replaced with a quartz fibre optics cross-section transformer, which feeds the light into a Spex Minimate grating spectrometer. An EMI 6256S PM extends the response into the ultra-violet. Photon counting is used and the spectrum is stored digitally in a computer. The relative efficiency of the system as a function of wavelength has been measured against a similar detection system, that has been calibrated using a radiometer calibrated from a black body source.

The electron beam is switched periodically from the area of interest onto an undeformed area, and counts from the two regions are stored separately. Subtracting these two spectra gives the luminescence of the plastic deformation alone, without any emission due to impurities. The background subtracted was small, but varied from sample to sample, whereas the form of the luminescence from the indentation did not vary. All spectra shown in this paper were taken in this fashion. In addition, the electron microscope allows a spectrum to be taken from an area of the order of one micron in size, allowing precise spatial location of the features in a spectrum.

2. Results

2.1. *MgO*

The total cathodoluminescence emission shows a picture-frame structure (c.f. ref. [1]). The etch pit distribution is fairly similar, so the luminescence is correlated with an area rich in dislocations.

Point defects are known to give rise to luminescence in these materials, and these can be generated by dislocation movement [2, 3]. Annealing at 850°C for 20 min should remove this contribution (e.g. ref. [2]). Fig. 1a shows a secondary electron micrograph of an area containing two cleaved indents. Fig. 1b shows the cathodoluminescence image before annealing, and fig. 1c shows the same area after annealing. The luminescence is little changed except at the very centre of the indentation, where luminescence is completely absent before annealing but very strong after annealing.

Spectra taken before and after annealing are shown in fig. 2. These were obtained from the same area and under the same conditions. The total emission intensity from this area did not change (within ±10%) after the annealing treatment, but the spectrum is considerably broadened, and a peak appears at 370 nm (this peak dominates the spectrum in the central bright region of the indentation).

This observation differs from that of Velednitskaya et al. [1], although the main features of our observations confirm theirs, and leads us to the conclusion that dislocations are primarily responsible for the cathodoluminescence, although of course point defects in the neighbourhood of the dislocations will affect it. The behaviour of the luminescence at the centre of the indentation can apparently be explained in two opposite ways: either there are no dislocations

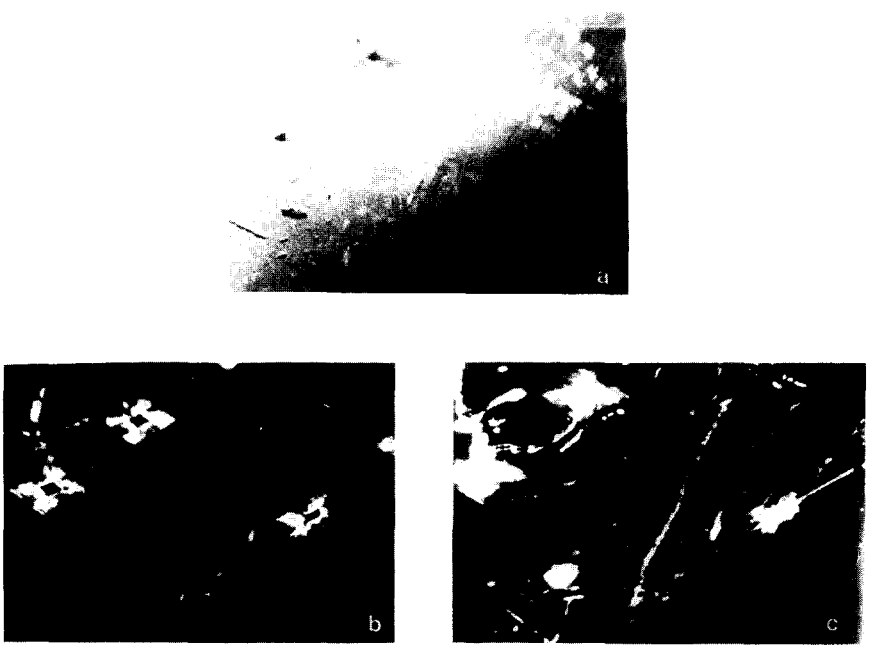

Fig. 1. Part of an array of hardness indents. The two indents in the lower right have been cleaved perpendicular to the surface of the crystal. (A) Secondary electron micrograph, (B) Cathodoluminescence before annealing, (C) Cathodoluminescence after annealing.

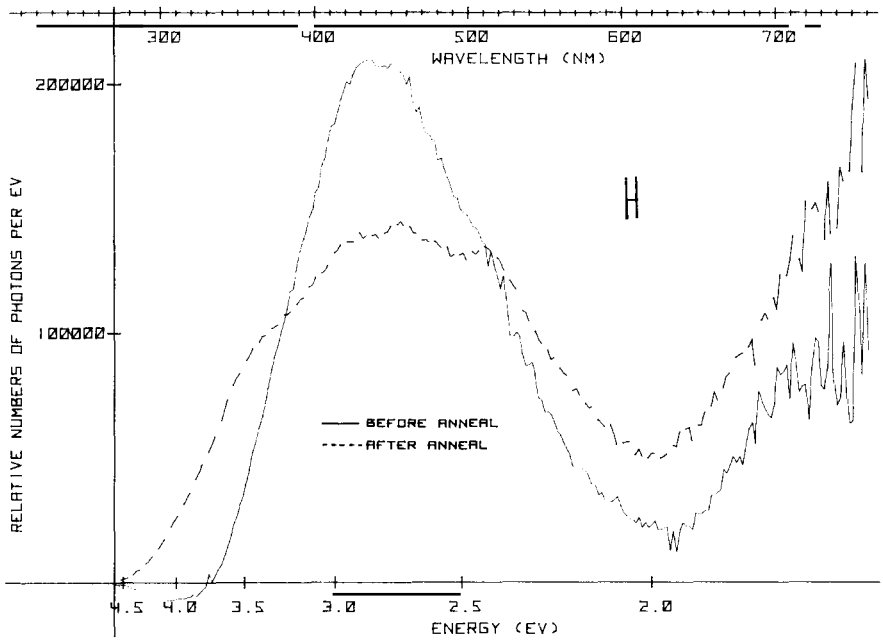

Fig. 2. The spectra of MgO corrected for instrument response.

present before the anneal, and some are introduced by the anneal (c.f. Velednitskaya et al. [1]); or the density of defects, both point defects and line defects, is very high before the anneal, causing the luminescence to be quenched, and the density is reduced by the anneal. Of the two explanations, the latter seems more likely.

2.2. *Diamond*

Conclusive evidence for the emission being due to dislocations comes from diamond. Dislocation networks in natural IIb diamond are visible in cathodoluminescence [4]. We have obtained a thin section of a diamond of this type and have looked at the cathodoluminescence on a HB5 scanning transmission electron microscope, which has also been modified for the detection of cathodoluminescence [5]. The signal levels are much lower, as a thin specimen is required for a simultaneous transmission electron image, so the signals are displayed in the form of line traces. Fig. 3 shows a line trace across a single dislocation and a strong peak in the luminescence is seen near the dislocation (which appears dark in the transmission electron signal). If the dislocation is tilted out of contrast in the electron signal, the luminescence peak is still observed. The peak cannot therefore be a diffraction effect and shows that the dislocation is an efficient site for recombination. A double peaked spectrum has been observed at low levels of X-ray excitation [6]; double-peaked spectra have also been observed in Ge [7] and Si [8].

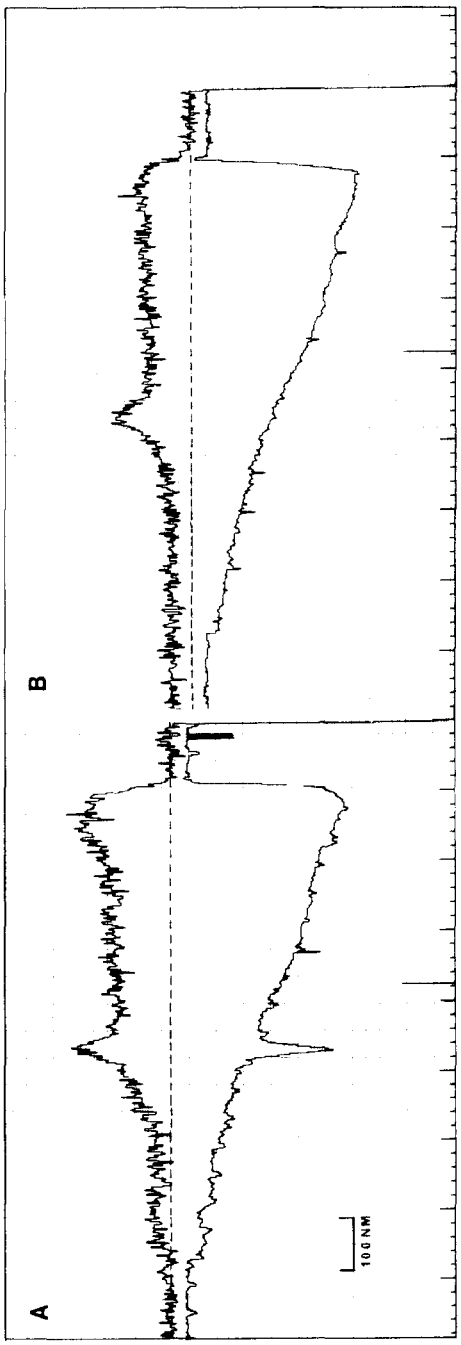

Fig. 3. Line traces across a single dislocation in diamond. The top trace is the cathodoluminescence signal; the dashed line shows the level of photomultiplier tube dark count. The lower trace is the bright field transmission electron signal. In (A) the dislocation is seen in the bright field image and in (B) it is tilted out of contrast.

3. Interpretation

Two models for the luminescence from dislocations are considered. Firstly, if there is considerable overlap between wave functions of centres along the core of the dislocation, then the centres will form a band, with a one dimensional density of states. This may show a double peaked spectrum under some conditions. The optical transitions on this model are polarised with the electric vector parallel to the line.

Secondly, the observed radiation could come from a highly perturbed band to band recombination. In the neighbourhood of a dislocation there will be a change in the energy of an electron or hole via the strain of the lattice. If V_0 is an electrostatic potential energy, the shift in this potential is given by $\delta V_0 \approx -V_0\epsilon$ where ϵ is the local dilatation due to the dislocation. The variation of ϵ with position is such that on one side of the dislocation core, there is strong compression, and on the other side, strong tension. Thus it is possible to have electrons and holes close together spatially, with their energies shifted towards each other. The total energy shift can be as much as 4 eV very close to the dislocation core in MgO. Thus the strong recombination (at fresh dislocations) at energies much lower than the fundamental gap, can be understood.

The emission from diamond is strongly polarised with the electric vector parallel to the line [9], while we have not detected polarisation from the MgO. This suggests that the emission from covalent materials be described by the one dimensional band model, while that from the ionic materials by the strongly perturbed band gap model.

Many features of the observations are still somewhat puzzling: for example, the dependence of the cathodoluminescent signal on excitation level, which is the same in MgO, diamond, and Ge: the low energy peak is reduced relative to the high energy peak as the excitation is increased. Clearly, observation of single dislocation images by scanning transmission electron microscopy can resolve some of these problems, although it seems unlikely that a spectrum can be obtained from a single dislocation.

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Note added in proof: The cathodoluminescence from the picture frame region in MgO can be entirely accounted for by dislocation luminescence, if their density is of the order of 10^{16} m^{-2} (as seems likely).