

Vacuum ultra-violet induced thermoluminescence in γ -irradiated and non-irradiated MgO powder

By Y. KIRSH, N. KRISTIANPOLLER and R. CHEN

Department of Physics and Astronomy,
Tel Aviv University, Tel Aviv, Israel

[Received 28 September 1976]

ABSTRACT

The effect of γ -irradiation at room temperature on MgO powder samples has been investigated by thermoluminescence (TL) methods. In addition to a TL peak at 516 K, 'persistent' changes in the properties of lower temperature TL peaks have been observed in the irradiated samples. This includes mainly an increase in the sensitivity to excitation in the vacuum U.V. region (115-170 nm) as well as the occurrence of TL excitation between 260 and 285 nm, which was hardly observable in the non-irradiated samples. The excitation maximum of the un-irradiated samples, at 118 nm (10.5 eV) seems to correlate with the prominent absorption peak at 10.8 eV, which has previously been attributed to an interband exciton. The structure in the 160-170 nm range of the excitation spectrum apparently corresponds to the previously reported exciton spectrum.

The γ -pre-irradiation also causes a shift of the TL peaks below 350 K towards lower temperatures. The experimental results provide new information regarding the processes involved.

§ 1. INTRODUCTION

Measurements of thermoluminescence (TL) in MgO have been reported by various authors. Most of these investigators concentrated on TL appearing after X-ray excitation. Thomas and Houston (1964) reported a TL peak at 410 K with an activation energy of 0.66 eV and, in some samples, a peak at 520 K with an activation energy of 0.9 eV. These peaks were bleachable by visible light between 1.8 and 3.2 eV. Wertz and Coffman (1965) suggested that the blue TL peak near 500 K, found after X-irradiation, results from the release of an electron from a Fe⁺ ion and its capture by a Cr³⁺ ion. Wertz, Hall, Helgeson, Chao and Dykoski (1967) found that a V⁻ centre releases a hole around 365 K, this hole being captured by a Cr²⁺ ion giving Cr³⁺ and red light emission. Searle and Glass (1968) found a TL peak at 351 K and attributed it to holes liberated with an activation energy of 1.13 eV and captured by Fe²⁺ ions, releasing blue emission. Most of the later researchers report such a mixture of blue and red TL which accompanies the release of holes from the V⁻ centre and their recombination according to the reactions :

- (1) $\text{Cr}^{2+} + \text{hole} \rightarrow \text{Cr}^{3+*} \rightarrow \text{Cr}^{3+} + h\nu$ (red) ;
- (2) $\text{Fe}^{2+} + \text{hole} \rightarrow \text{Fe}^{3+*} \rightarrow \text{Fe}^{3+} + h\nu$ (blue).

According to Wertz *et al.* (1967) most of the Cr ions in MgO before X-irradiation are trivalent, but most of the Fe ions are divalent. The X-irradiation induces

valence changes from Cr^{3+} to Cr^{2+} and from Fe^{2+} to Fe^{3+} and Fe^+ . Hecht and Taylor (1967) excited their polycrystalline MgO samples at liquid nitrogen temperature (LNT) and found a series of TL peaks between 112 and 500 K with a major one at 355 K, and calculated their activation energies assuming first-order kinetics. Chao (1971) found a peak at 367 K with an activation energy of 0.8 eV and investigated the details of the red emission. Takeuchi, Inabe and Nanto (1975) recorded a main peak also at 367 K and found that the kinetics order was concentration dependent, changing from 1.3 for high Fe contents to second-order for low Fe concentration. In a recent paper (Takeuchi, Inabe and Nanto 1976) the kinetics order of the red TL components was investigated.

TL as well as thermally stimulated conductivity (TSC) in U.V. excited MgO single crystals have been reported by Yamaka (1954), who found similar curves after irradiation with mercury light and X-rays at RT. He found TL peaks at 338, 350, 368 and 473 K with activation energies ranging from 0.56 to 1.35 eV. Hansler and Segelken (1960) excited MgO samples with 4.9 eV U.V. light and found TL peaks at ~ 343 and 430 K. Ziniker, Mellow and Mueller (1972) found red and orange TL peaks after monochromatic U.V. excitation between 220 and 380 nm and identified main TL peaks at 350, 380 and 460 K.

TL and TSC in γ -irradiated MgO crystals were investigated by Mallard and Crawford (1969, 1972), a main peak was reported at ~ 360 K with an activation energy of 1.1 eV. When cycles of heating and cooling were performed, values of activation energies between 0.73 and 1.57 eV were found in the temperature range between 294 and 473 K.

Pollard, Bowler and Pomerantz (1965) reported TSC in electron bombarded MgO. Sibley, Kolopus and Mallard (1969) reported a major TL peak at 361 K after irradiation, in addition to two smaller peaks at 408 and 480 K appearing in the 'as grown' samples. In a recent paper, Carter (1976) reports the excitation of MgO doped with Ni, using a ^{60}Co γ -ray source which yields a main peak at 480 K (when the heating rate is rather high, about 58 K/min). MgO has also been used (Ritz and Attix 1973) as a fast neutron dosimeter using its TL and thermally stimulated electron emission properties. A main TL peak appeared at ~ 360 K under these conditions.

Some of these properties of MgO, including TL and TSC, have been summarized in two review articles, by Sonder and Sibley (1972) and by Hughes and Anderson (1972). A short summary of TL peaks and their activation energies has been given by Ziniker, Rusin and Stoebe (1973).

The present paper reports and discusses the result of experiments performed on MgO powder samples. Our investigations extended the above mentioned ranges of excitation as follows :

- (1) TL peaks were recorded after U.V. excitation at LNT, thus enabling the observation of U.V. excited TL peaks below RT.
- (2) The U.V. excitation was extended to the vacuum (V.U.V.) region, up to ~ 11 eV, and revealed new information.
- (3) Differences between U.V. excited TL in γ -irradiated and non-irradiated samples were investigated. The results enable the distinction between traps created by γ -rays, and the filling of existing traps by carriers.

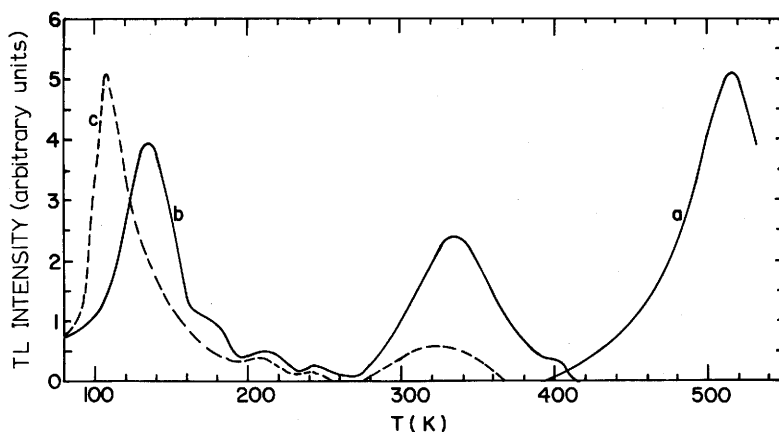
§ 2. EXPERIMENTAL

The MgO powder was the same as that commonly used for insulation of cables and was supplied by Norton Company. The irradiated sample was exposed at RT to a ^{60}Co γ -ray irradiation facility for 65 hours at a rate of 0.3 Mrads/hour. Thus the total dose was ~ 20 Mrads. The sample was held at RT for over a year prior to the TL measurements. The powder samples were glued on to $1 \times 1 \text{ cm}^2$ aluminium plates using 'water glass' (sodium silicate solution); the thermoluminescence of the water glass under similar irradiation conditions of vacuum U.V. has been checked and found negligible (as compared to the thermoluminescence of the γ -irradiated and the non-irradiated MgO). The samples were kept in a vacuum cryostat connected to a 1 m normal incidence vacuum U.V. monochromator (McPherson 225) with a linear dispersion of 8.3 \AA/mm . The samples were irradiated at 80 K by monochromatic U.V. light in the range 110–300 nm. The light source was a 1000 W hydrogen arc lamp, and the width of the monochromator slits was usually 1 mm. A screen of sodium salicylate monitored the exciting light and allowed us to irradiate the samples at various wavelengths with constant photon flux. During heating the irradiated samples at a constant heating rate of 10 K/min, the TL was detected by an EMI 6256S photomultiplier, connected to a Keithley 410 micro-microammeter. The glow curves were recorded on an x - y recorder, the x -axis giving the temperature of the sample, as measured by a copper-constantan thermocouple.

§ 3. RESULTS

Figure 1 shows representative glow curves measured in this work. Since the γ -irradiated samples were held at RT for over a year before the heating, no peak was observed below 400 K in the curve measured during the first heating

Fig. 1



TL glow curves of MgO powder samples : (a) TL observed during the first heating cycle of a γ irradiated sample ; (b) V.U.V. excited TL of a non-irradiated sample ; (c) V.U.V. excited TL, after γ -irradiation at RT and heating to above 550 K.

cycle. This is shown in curve (a), in which a very intense peak at 516 K appears (the scale is reduced by a factor of 40 to accommodate this curve into the same graph with curves (b) and (c)). Curve (b) is representative of the V.U.V. excited TL of the samples which were not γ -irradiated. Main peaks appear at 135 and 334 K, with minor peaks at 210 and 240 K and a shoulder at 180 K. This curve has essentially the same features as the X-ray excited TL curve given by Hecht and Taylor (1967). Curve (c) gives the TL of γ -irradiated samples after heating to 550 K and V.U.V. excitation at LNT. The lowest temperature peak is seen to be stronger in the γ -irradiated samples and the other peaks are smaller. All the peaks are shifted to lower temperatures as compared to the non-irradiated samples, the low temperature peak from 135 to 108 K and the high temperature one to 320 K. Below 400 K curve (c) was essentially the same, independent on whether the γ -irradiated samples had been pre-heated to ~ 550 K or not. This seems to exclude a direct connection between the changes in the lower temperature peaks and the defects related to the 516 K peak.

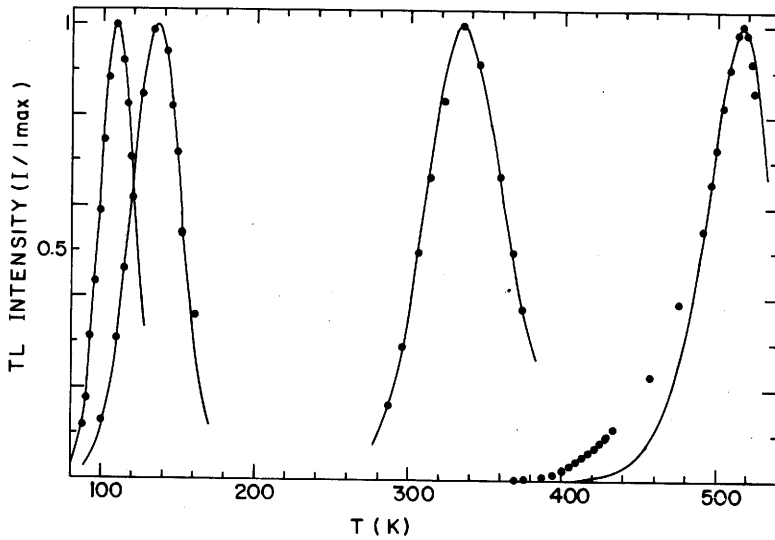
The peaks at 108, 135, 334 and 516 K were analysed using a curve fitting method (Shenker and Chen 1971) which yields the activation energy and the kinetic order of the peaks. The results are given in the table whereas the theoretical curves fitted to the experimental results are shown in fig. 2. It is to be noted that the peaks in fig. 2 are all normalized to give a maximum intensity of unity. The 516 K peak was fitted for $T > 490$ K only. A different activation energy is found using the initial rise method, indicating the occurrence of another glow peak around 440 K. The kinetics of the three upper peaks is second order. The 135 K peak seems to have first-order kinetics. This is similar to the result of Takeuchi *et al.* (1975) for the 367 K peak and that of Searle and Glass (1968) for the 351 K peak which, as will be discussed below, may both correspond to the peak we observe at 334 K.

Parameters of the glow peaks in MgO. T_m (K) is the temperature of the maximum, E (eV) are the activation energies as evaluated by initial rise and best fit methods; l is the order of the kinetics.

T_m (K)	E (eV) (initial rise)	E (eV) (best fit)	l	Irradiation
108	0.10	0.12	2	γ +U.V.
135	0.08	0.10	1-1.3	U.V.
334	0.47	0.52	2	U.V., or γ +U.V.
~ 440	1.02	—	—	γ
516	—	1.13	2	γ

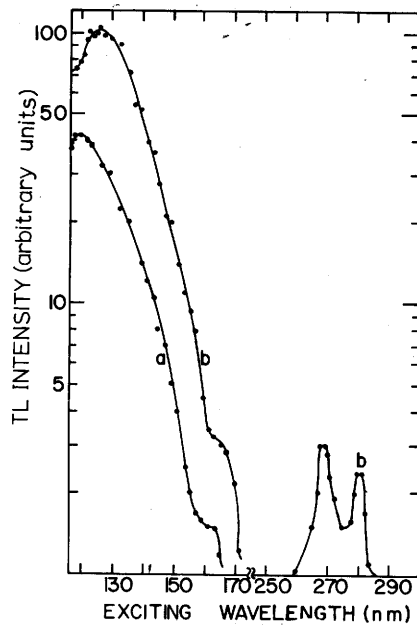
Figure 3 shows on a semilog scale the TL excitation spectrum; namely, the relative efficiency of various U.V. wavelengths for exciting the γ -irradiated (curve b) and non-irradiated (curve a) samples. For the non-irradiated sample the efficiency has a maximum at 118 nm (10.5 eV) and is lower compared to the γ -irradiated sample. In the pre-irradiated samples the maximum shifts

Fig. 2



Fitting of the measured TL peaks (dots) to the theoretical expression of general order kinetics (TL intensities are normalized to the maximum intensity (I_{max}) of each peak).

Fig. 3



TL excitation spectrum of (a) non-irradiated and of (b) γ -irradiated MgO powder.

to 125 nm (10 eV). Additional excitation maxima appear in this curve at 268 and 280 nm, which were hardly observable in the non-irradiated samples.

§ 4. DISCUSSION

The new information described in this paper is related to 'persistent' changes caused by γ pre-irradiation and observed after U.V. excitation. Since excitation was at LNT, observation of additional TL peaks below RT was possible. This has been done before by Hecht and Taylor (1967), but in their case for X-ray excitation only. The peak appearing at 516 K is similar to that described in previous works, e.g. Hecht and Taylor (1967) and Thomas and Houston (1964). The fact that the peak which usually appears around 350 K is not seen here in the pre-irradiated samples can easily be explained as a result of holding the sample before the measurement for a long time at RT.

By the term 'persistent' we mean that curves similar to (c) in fig. 1 were found in the γ -irradiated samples even when the cycles of V.U.V. excitation at LNT and heating to about 550 K were repeated several times. Comparison with previous works suggests that the TL is related to changes in the valence of Fe and Cr impurities, and that the peak is related to the release of a hole from a V^- centre. This, however, should not be considered as a destruction of the vacancy centre since, as pointed out by Tench and Duck (1973), the cation vacancy is destroyed only between 650 and 700 K, with an activation energy of 2.7 eV. As for the traps responsible for the lower temperature peaks. We suggest that these are due to other V hole centres which may involve impurity ions.

The shift of all four peaks to lower temperatures after the γ irradiation is explained as follows. It is quite well known that first-order peaks do not change their temperature for various excitation doses whereas non-first-order peaks (including second-order peaks) shift to lower temperature at high doses. Our peaks definitely show second-order characteristics, excluding the 135 K peak whose order is between 1 and 1.3. This, however, does not constitute a full explanation of the effect since usually, in non-first-order peaks, the change in temperature with higher doses is accompanied by an increase in the intensity of the peak, which is not the case here. It has been shown (Chen 1971) that, while considering the relation between a TL peak and its corresponding peak $n_c(t)$ of free carriers in the band (which is directly related to the TSC curve), one gets the condition for the TL maximum as

$$\left(\frac{dn_c}{dt}\right)_{T_{\max}} = A[n_c(T_{\max})]^2. \quad (1)$$

Here A is the 'recombination probability' ($\text{cm}^3 \text{sec}^{-1}$) which is considered to be constant and T_{\max} is the temperature at which the TL peak reaches its maximum. This equation shows that the TL maximum occurs when $dn_c/dt > 0$ which means that the TL maximum appears at a lower temperature than its TSC counterpart. Another important feature of eqn. (1) is that m_0 , the initial filling of the recombination centres does not appear, therefore changes in the occupancy of the recombination centre (with the dose) would not change T_{\max} . This case is an extension, in this special sense, to the first-order behaviour. The fact that in our case the peaks shift with the prior γ -irradiation indicates that this irradiation influences the concentration of the traps (various

V centres). The fact that the peaks shift to lower temperature at higher irradiation doses is qualitatively explained as follows. Suppose that the γ irradiation results in a higher concentration of traps which in turn results in higher values of n_c and suppose that the curve of $n_c(t)$ increases without substantially changing its shape (no substantial distortion in the $n_c(t)$ peak). For the γ -irradiated sample, the right-hand side of eqn. (1) would increase much faster (since it contains n_c^2) than the left-hand side. In order that the condition (1) remains valid, the TL peak should shift further towards lower temperatures. This would both decrease the right side of the equation and increase the left side until they become equal as required. This shift represents a 'second-order like' behaviour. The fact that the intensity of the lowest temperature peak increases, along with relatively large shift of its temperature may be related to the fact that the shallowest trap is more abundant in the γ -irradiated sample. The total area under curves (b) and (c) seems to be governed by the recombination centres which are not changed by the γ -irradiation. Thus, since the first peak 'consumed' more of the carriers in the recombination centres, the other glow peaks are lower in the γ -irradiated samples.

The part of the glow curve appearing below RT can be compared only to the work of Hecht and Taylor (1967). As mentioned above, the general shape of the curve is similar, the differences being possibly attributable to the fact that their samples were irradiated by X-rays whereas ours were irradiated by V.U.V. The possibility of differences in the samples, which do not come from the same source, should also be taken into account. The very intense peak at 516 K corresponds to a similar peak (though not so intense) reported previously by Hecht and Taylor (1967) at 500 K and by Thomas and Houston (1964) at 520 K. The dominant peak which was found by various authors to appear at different temperatures between 350 and 400 K, occurs in the present work at 334 K in the non- γ -irradiated samples and shifts to 320 K in the irradiated ones. The differences in the peak temperatures in various works can be attributed to differences among the samples, various heating rates and, as mentioned by Wertz *et al.* (1967), the lack of good thermal contact between the sample and the thermocouple measuring its temperature. The relatively lower temperature in our work seems to be due to the fact that we used a powder sample glued onto a metal plate thus enabling good heat transfer and therefore, probably a more reliable measure of the peak's maximum. A bad thermal contact can also distort the shape of the peak since various parts of the sample are at different temperatures and therefore at different stages along the true glow curve. This may also cause errors in evaluation of the activation energies and may at least partly account for the big difference between the usually reported values of ~ 1.0 eV (Ziniker *et al.* 1973) and our value of ~ 0.5 eV. It is to be noted that some of the previous authors (e.g. Yamaka 1954, Hecht and Taylor 1967) assumed a certain frequency factor s to calculate the activation energies. The lower the assumed value of s , the lower E becomes. In our method of curve fitting, no such assumption was necessary. As seen in the table, the peak near 330 K as well as the 110 and 516 K peaks, were found to be of second order. The effective frequency factor (for the meaning of the effective frequency factor for a non-first-order case, see Chen (1969)), was found to be low, around 10^5 sec $^{-1}$. The very good agreement between the

experimental and theoretical curves, supports the present results. The fitting of the 516 K peak was made using only the higher intensity points, yielding $E = 1.3$ eV, since the experimental results indicate the existence of another peak at ~ 440 K. The activation energy of the latter was found, using the initial rise method, to be 1.02 eV.

The curves given in fig. 3 are the excitation spectra of the 108–134 K TL peaks. The structure appearing in the γ -irradiated samples between 260–285 nm, corresponds quite well to the structure in the TL excitation reported previously (Ziniker *et al.* 1972). The excitation of TL in the γ -irradiated samples by photons of this energy indicates that the irradiation creates centres which remain unchanged since we do not heat the sample above 525 K. These can be filled with holes by the U.V. excitation and emptied by the heating. Traces of excitation in this range in the non-irradiated samples were also observed in our work, indicating that the traps introduced by the γ -irradiation exist, though in much smaller concentration, in the unirradiated samples. The excitation in this region was attributed by Ziniker *et al.* (1972) to Fe, Cr and Mn ions which, as mentioned above, probably form the recombination centres. The difference between γ -irradiated and non-irradiated samples seems to result from the high or low concentration of traps (V_A centres), respectively. In the γ -irradiated samples, these centres are more abundant, and the U.V. irradiation can fill them with holes.

An alternative explanation might be a process of photo-transfer (Stoddard 1960). According to this, the γ -irradiation fills deep traps which can thermally release carriers at temperatures much above 500 K. The subsequent U.V. illumination at LNT may transfer charge carriers from these deep traps to shallower ones and thus cause the appearance of TL below RT. This explanation does not seem, however, likely in the present case, since V.U.V. photons of energies higher than the band gap (8.7 eV) should also fill the deep traps, in a way similar to the γ -irradiation. One would therefore expect changes in the TL produced by, say, 270 nm U.V. light, after pre-irradiation with ~ 10 eV photons. This has not been observed.

The structure in the 160–170 nm range seems to correspond to the exciton spectrum reported by Roessler and Walker (1967). These investigators measured the reflectance from MgO crystals in the U.V. and found a few maxima in the 7.6–7.8 eV range. In our case this structure is superimposed on the general increase in the TL excitation spectrum towards lower wavelengths. This indicates that the creation and filling of centres by U.V. light may be due, in part, to the creation of excitons which subsequently decay to electrons and holes. It is of interest that no special feature is seen at ~ 143 nm which corresponds to the usually accepted value of 8.7 eV for the forbidden gap. The curve for the non-irradiated sample reaches a maximum at 118 nm (10.5 eV) which may correspond to the 10.8 eV absorption peak which seems to be due to an intraband exciton (Walch and Ellis 1973). We do not have a satisfactory explanation for the fact that the excitation maximum shifts to ~ 10 eV in the γ -irradiated samples.

ACKNOWLEDGMENT

We should like to thank Dr. G. F. Lynch from the Applied Physics Division, Chalk River Nuclear Laboratories, Ontario, Canada and Professor M. Sayer

from the Physics Department, Queen's University, Kingston, Ontario, Canada for providing the γ -irradiated and non-irradiated samples.

REFERENCES

- CARTER, A. C., 1976, *Nature, Lond.*, **260**, 133.
 CHAO, C. C., 1971, *J. Phys. Chem. Solids*, **32**, 2517.
 CHEN, R., 1969, *J. electrochem. Soc.*, **116**, 1254 ; 1971, *J. appl. Phys.*, **42**, 5899.
 HANSLER, R. L., and SEGELKEN, W. G., 1960, *J. Phys. Chem. Solids*, **13**, 124.
 HECHT, H. G., and TAYLOR, E. D., 1967, *J. Phys. Chem. Solids*, **28**, 1599.
 HUGHES, A. E., and HENDERSON, B., 1972, *Point Defects in Solids*, Vol. I, edited by J. H. Crawford, Jr. and L. M. P. Slifkin (London, New York : Plenum Press), p. 451.
 LYNCH, G. F., 1975, *Can. J. Phys.*, **53**, 210.
 LYNCH, G. F., and SHIELDS, R. B., 1974, Report No. AFCL-4827 (Chalk River : U.S.A. : Atomic Energy of Canada Ltd.).
 MALLARD, W. C., and CRAWFORD, J. H., Jr., 1969, *Solid St. Commun.*, **7**, 1767 ; 1972, *J. appl. Phys.*, **43**, 2060.
 POLLARD, J. H., BOWLER, D. L., and POMERANTZ, M. A., 1965, *J. Phys. Chem. Solids*, **26**, 1325.
 RITZ, V. H., and ATTIX, F. H., 1973, *Appl. Phys. Lett.*, **23**, 166.
 ROESSLER, D. M., and WALKER, W. C., 1967, *Phys. Rev.*, **159**, 733.
 SEARLE, T. M., and GLASS, A. M., 1968, *J. Phys. Chem. Solids*, **29**, 609.
 SHENKER, D., and CHEN, R., 1971, *J. Phys. D*, **4**, 287.
 SIBLEY, W. A., KOLOPUS, J. L., and MALLARD, W. C., 1969, *Phys. Stat. Sol.*, **31**, 223.
 SONDER, E., and SIBLEY, W. A., 1972, *Point Defects in Solids*, Vol. I, edited by J. H. Crawford, Jr. and L. M. P. Slifkin (London, New York : Plenum Press), pp. 264, 265.
 STODDARD, A. E., 1960, *Phys. Rev.*, **120**, 114.
 TAKEUCHI, N., INABE, K., and NANTO, H., 1975, *Solid St. Commun.*, **17**, 1267 ; 1976, *Phys. Stat. Sol.*, **33**, K125.
 TENCH, A. J., and DUCK, M. J., 1973, *J. Phys. C*, **6**, 1134.
 THOMAS, B., and HOUSTON, E., 1964, *Br. J. appl. Phys.*, **15**, 953.
 WALCH, P. F., and ELLIS, D. E., 1973, *Phys. Rev. B*, **8**, 5920.
 WERTZ, J. E., and COFFMAN, R. E., 1965, *J. appl. Phys.*, **36**, 2959.
 WERTZ, J. E., HALL, L. C., HELGESON, J., CHAO, C. C., and DYKOSKI, W. S., 1967, *Interaction of Radiation with Solids : 1966 Cairo Conference*, edited by E. Bishay (New York : Plenum Press), p. 617.
 YAMAKA, E., 1954, *Phys. Rev.*, **96**, 293.
 ZINIKER, W. M., MERROW, J. K., and MEULLER, J. I., 1972, *J. Phys. Chem. Solids*, **33**, 1619.
 ZINIKER, W. M., RUSIN, J. M., and STOEBE, T. G., 1973, *J. mater. Sci.*, **8**, 407.