Site occupation in gadolinium-doped calcium tungstate

J. S. THORP, E. A. E. AMMAR
Department of Applied Physics and Electronics, University of Durham, UK

The electron spin resonance spectrum of the S-state ion Gd^{3+} in a calcium tungstate host lattice has been examined at 37.5 GHz over the temperature range 290 K to 4.2 K. Low concentration Czochralski-grown single crystals having gadolinium concentrations of about 100 ppm were used to ensure substitution by Gd^{3+} in calcium sites; the crystals were vacancy compensated. Although the general features of the 290 K spectrum agreed well with that reported previously by Hempstead and Bowers, extra lines were observed very close to the main $\Delta M = 1$ transitions. Examination in the ϕ-plane showed that the extra lines were most pronounced near $\phi = 55°$ and that their intensites relative to those of the main transitions increased as the temperature was reduced. The extra lines are explained in terms of the ordering of oxygen vacancies.

1. Introduction

There is a considerable volume of evidence to support the view that, at low concentrations, gadolinium enters the calcium tungstate lattice by substitution at calcium sites. In recent measurements of spin–lattice relaxation in $Gd^{3+}/CaWO_4$ however, Thorp, Buckley and Brown [1] observed that at helium temperatures the main Gd transitions contained two components which were separated by about 2 mT and had slightly different relaxation rates. The aim of the present study was to investigate the cause and nature of the additional components near to the main $\Delta M = 1$ gadolinium transitions since the first observations had suggested that they were different in kind from those to be expected from gadolinium substituted at tungsten sites.

Calcium tungstate, (scheelite), crystallizes in the tetragonal system [2] and has a space group C_{4h}^6 ($I4_1/a$) with four molecules to the unit cell [3]. The lattice parameters are $a = b = 3.243$ Å and $c = 11.376$ Å. Fig. 1 shows the unit cell with the oxygen atoms omitted for clarity. The unit cell may be divided into four horizontal (0 0 1) layers of equal stacking density. Arbel and Stokes [4] reported that cleavage and slip occur parallel to these layers in $CaWO_4$. Each calcium atom is surrounded by eight oxygen atoms at an average distance of 2.46 Å in the shape of a distorted cube. The four calcium sites are equivalent in pairs, one pair being derived from the other by body centering about a calcium site as reflected in the (0 0 1) plane. This is shown in the projection of the eight oxygen atoms on the (0 0 1) plane through the calcium atom for the two sites, Fig. 2.

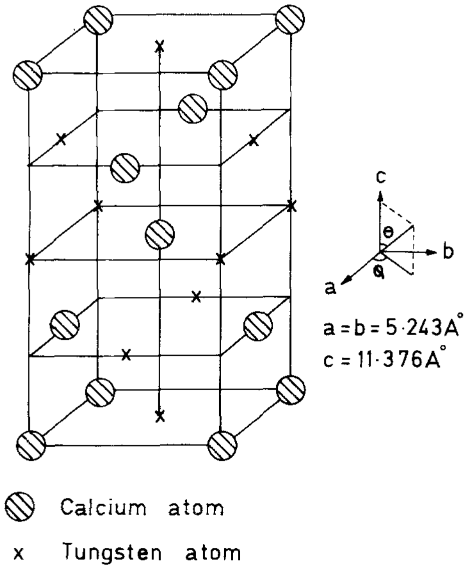

Figure 1 The unit cell of $CaWO_4$ (scheelite) with oxygen atoms omitted for clarity.

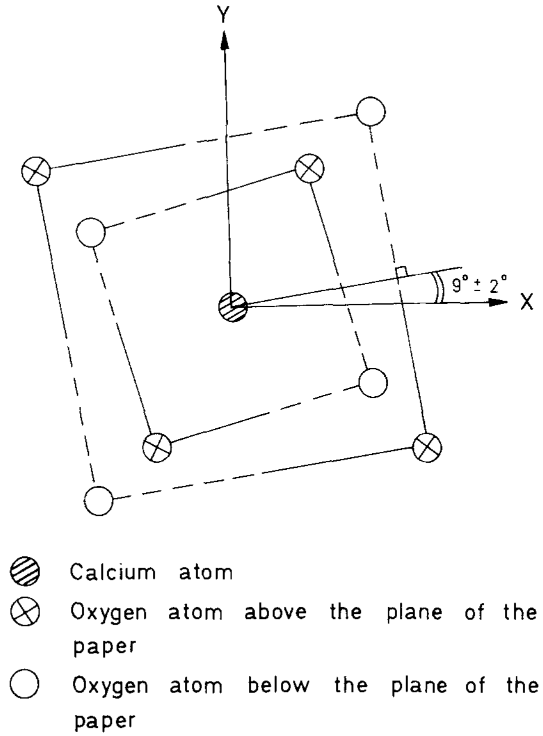

Figure 2 A projection of the eight neighbouring oxygen atoms on the (0 0 1) plane through the calcium atom for the two sites which are related to each other by reflection in the plane of the paper.

The tungsten atom is surrounded by four oxygen atoms in the same WO_4 group, nearly tetrahedral [5] with a bonding distance 1.784 Å. The site symmetry of both the Ca and W atoms in $CaWO_4$ is S_4. The distorted cube of oxygen atoms surrounding the Ca^{2+} site is twisted at an angle of about $9° \pm 2°$ from the unit cell a-axes in the (0 0 1) plane. These surrounding oxygens provide the framework of the crystal field symmetry at the Ca^{2+} site, the direction of which was first determined by Hempstead and Bowers [3] and was confirmed recently by Buckley [6]. This property was used to identify the sense of the $+z$-axis in $Gd/CaWO_4$ crystals for alignment in ultrasonic experiments made by Farley [7, 8].

The trivalent gadolinium ion has seven unpaired electrons in the 4f unfilled shell which make it half-filled and give rise to a ground state $(4f^7)^8S_{7/2}$. As an S-state ion, gadolinium should exhibit no first-order crystal field splitting, a feature discussed by Bleaney and Stevens [9]. However, ESR experiments on Gd^{3+} have shown that small splittings do exist and their magnitudes in crystals of the scheelite series were reported by Vinokurov *et al.* [10]. These authors gave crystal field splitting constants b_2^0 for $Cd/CaWO_4$ at 77 K and 290 K as $916.7 \times 10^{-4}\,cm^{-1}$ and $892.4 \times 10^{-4}\,cm^{-1}$, respectively. This is in exact agreement with the value of b_2^0 at 77 K given by Hempstead and Bowers [3]. A suggestion that the splittings were due to a spin–spin interaction was made by Abragam and Price [11]. Their idea was that in the crystal field, even though the ion is in an S-state, there will be some distortion of the orbits resulting in the charge cloud becoming slightly ellipsoidal. The dipole–dipole energy of the spins varies with their orientation with respect to the axes of the ellipsoid, and thus the eigenvalues depend on the spin orientation. On this basis, in the tetragonal field of calcium tungstate, the $J = 7/2$ state splits into four Kramers' doublets and paramagnetic resonance can then occur between the Zeeman levels of these four doublets. The energy level diagram for Gd^{3+} in calcium tungstate at 35.5 GHz was drawn by Buckley [6] using straight line extrapolation from the data predicted by Harvey and Kiefte [12] for 9 GHz. Convincing agreement with theory was shown by Buckley's experimental results and those of several other workers including especially the data given by Dernov-Pegarev *et al.* [13] for $Gd/CaMoO_4$. The ESR spectrum of only seven lines for $\Delta M = 1$ transitions, which was observed by Thorp *et al.* [14] in their study of dipolar broadening mechanisms in $Gd^{3+}/CaWO_4$, gives further evidence for Gd^{3+} substitution at Ca^{2+} sites in a tetragonal symmetry.

2. Experimental

The specimens examined in the present study were the same as those which had previously been used for the relaxation time studies, i.e. they were single crystal boules of $CaWO_4$ doped with Gd, grown by the Czochralski technique by I.R.D. Ltd., Newcastle upon Tyne, with the c-direction along the growth axis. As it had been reported by Nassau and Broyer [15] that the melting point was about 1600° C, this temperature was used for growth. Gadolinium was added in the form of the oxide Gd_2O_3 to the powdered calcium tungstate. In pulling from the melt, trivalent rare earths can be incorporated (without the presence of a univalent ion), by vacancy compensation. As a rare earth ion, gadolinium substitutes at the calcium sites [15] giving rise to one calcium vacancy for each pair of gadolinium ions to maintain local charge neutrality; all the specimens used here were vacancy compensated. The nominal doping levels used were 0.005, 0.01 and 0.05 at.% although independent analysis (by the Analytical Services Laboratory, Imperial College) showed that the actual levels were all less than about 100 p.p.m. This concentration level was well below that at which substitution at W sites has been reported by Kedzie and Kestigian [16]. The very compact nature of the structure of $CaWO_4$ makes the interstitial sites very unlikely. Thus, in the material examined, the strongest probability was that the gadolinium would have entered the lattice substitutionally at calcium sites.

All the ESR measurements were made with a 35.5 GHz spectrometer. The crystals were oriented in the spectrometer cavity so that the majority of the spectra were obtained at temperatures between 270 K and 4.2 K, with the d.c. magnetic field in the ϕ-plane. Examination of the specimens by both optical, microscopic and X-ray Laue techniques had shown that the crystalline perfection was very high and that there was no detectable mosaic structure present.

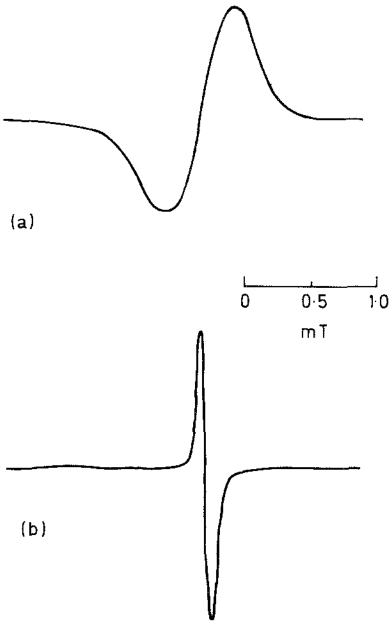

Figure 3 Derivative line-shape of a clean $\Delta M = 1$ transition at (a) 293 K and (b) 4.2 K; (0.005% $Gd/CaWO_4$, 35.5 GHz, $\phi = 0°$).

3. Results

The general features of the Gd^{3+} spectrum were in close agreement with those reported by Hempstead and Bowers [3]. In $CaWO_4$ all four possible positions of the Ca^{2+} in the unit cell possess a local crystal field symmetry of S_4 and are magnetically equivalent. This leads to the same single spectrum for each paramagnetic ion introduced into the host lattice and the spectrum was reported by Hempstead and Bowers [3] as consisting of seven widely spaced strong lines due to $\Delta M = \pm 1$ and a number of weaker transitions corresponding to $\Delta M = \pm 2$, (such transitions are to be expected as b_0^2 is so large as to be comparable with $g\beta H$). They also observed that other weak lines, which represent the hyperfine structure due to the odd Gd isotopes (^{155}Gd 14.7% abundance; ^{157}Gd 15.7% abundance) flanked the strong ones; both isotopes have nuclear spin $I = 3/2$ and each hyperfine component has only about 5% of the intensity of the main line. Here, we will designate the $\Delta M = \pm 1$ transitions due to the even isotopes as clean lines, a clean line being defined as one characteristic of tetragonal symmetry, appearing as a single symmetrical, well-balanced signal on the derivative output. Such a spectrum is obtained with the 0.005 at.% Gd sample, and one of the transitions, observed with the magnetic field H parallel to the crystallographic a-axis in the (0 0 1) plane (i.e. with $\phi = 90°$ and $\phi = 0°$), is reproduced in Fig. 3. The line is clean and the transition remains so at room temperature, 77 K and 4.2 K. This form of line-shape was also observed for all the Gd transitions over a wide range of angles ϕ except near $\phi = 55°$. Near this angle some distortion in line-shape was observed. This distortion became more pronounced as the temperature of the sample was lowered when it resembled a splitting of each transition. These effects are illustrated by the spectra shown in Fig. 4. The splitting effect was first observed in the first quadrant (i.e. in the ϕ-plane with $0 < \phi < 90°$, and the $+z$-axis is upwards perpendicular to the plane of observation); measurements were extended to the other quadrants and it was found that the splittings were very much more pronounced in the first and third quadrants than in the second and fourth. With the higher concentration sample (0.05 at.% Gd) the splitting was observed over a much wider range of angles ϕ, as was reported by Buckley [6]. This is shown in Fig. 5. The derivative plots were integrated, and analysis of these confirmed that the main new experimental observations were: (a) the occurrence of an extra line spaced up to a linewidth away from each $\Delta M = 1$ transition; (b) the prominence of the extra component at certain polar

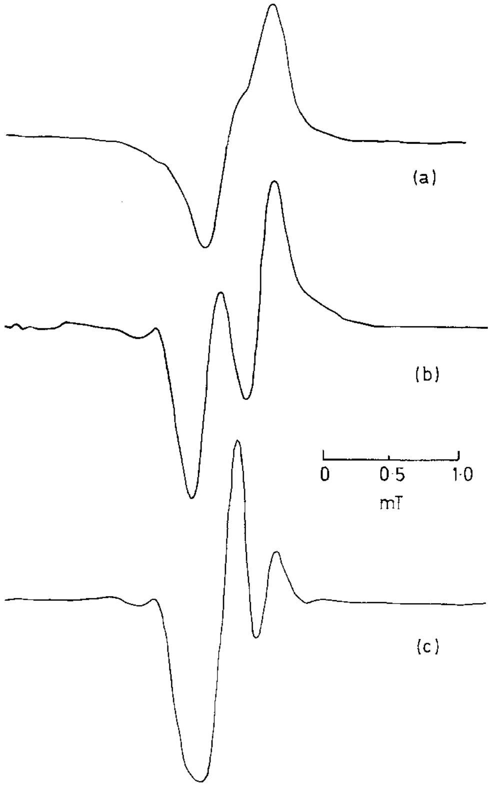

Figure 4 Derivative line-shapes of $\Delta M = 1$ transition in 0.005% Gd/CaWO$_4$ at (a) 293 K, (b) 77 K and (c) 4.2 K; $\phi = 55°$, 35.5 GHz.

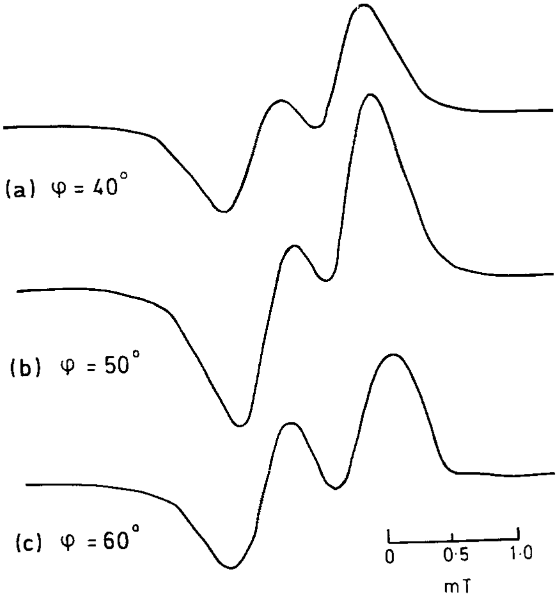

Figure 5 Derivative line-shapes of $\Delta M = 1$ transition in 0.05% Gd/CaWO$_4$; (77 K, 35.5 GHz).

angles; and (c) the relative increase in the intensity of the extra component (as compared to the main $\Delta M = 1$ transition) as the temperature was reduced from 290 K to 4.2 K.

4. Discussion

The literature contains a number of references to extra lines observed in the ESR spectra of doped calcium tungstate. These extra lines may be considered as falling into four groups whose features are summarized below:

(a) Transitions due to various compensation mechanisms for the excess charges which arise from doping the host scheelites with trivalent rare earth ions in order to achieve charge neutrality. The published ESR data indicated the presence of centres of lower symmetry in addition to tetragonal centres. Three non-tetragonal centres in Er^{3+}-doped samples and two such centres in Tb^{3+}-doped crystals were reported by Abdulsabirov *et al.* [17]. These authors concluded that all the published information on non-tetragonal Ce^{3+} (Mims *et al.* [18], Volterra *et al.* [19]), Nd^{3+} (Garrett and Merrit [20]) and Yb^{3+} (Ranon and Volterra [21]) together with their own data on the non-tetragonal Tb^{3+} centres in CaWO$_4$ can be interpreted on the assumption that the compensating defects are located in one of three positions denoted by I, II, III in the projection shown in Fig. 6. The "strongest" non-tetragonal centres are formed when a compensating defect (such as a Na$^+$ ion or a Ca^{2+} vacancy for crystals grown with and without sodium compensation, respectively) is located at the Ca^{2+} site nearest to the trivalent ion (Position I in Fig. 6). These additional non-tetragonal centres have different parameters and *g*-values; in other words, they would appear in the ESR spectra at different field positions from those of the normal tetragonal transitions.

(b) As Kedzie and Kestigian reported [16], substitution would occur at W^{6+} sites as well as Ca^{2+} sites either with or without adding Na$^+$ ions for charge compensation. A spectrum of five main lines (plus smaller lines due to hyperfine structure) was observed for Nd^{3+}/CaWO$_4$ crystals. The central line of the five transitions was the most intense and was attributed to Nd^{3+} in the Ca site, while the four remaining lines were thought to be due to Nd^{3+} ions in a W site. Although Garrett and Merritt [20] and Ranon and Volterra [21] found that the chemical evidence argues strongly for the substitution of Nd^{3+} in Ca sites, we still regard substitution of rare earth

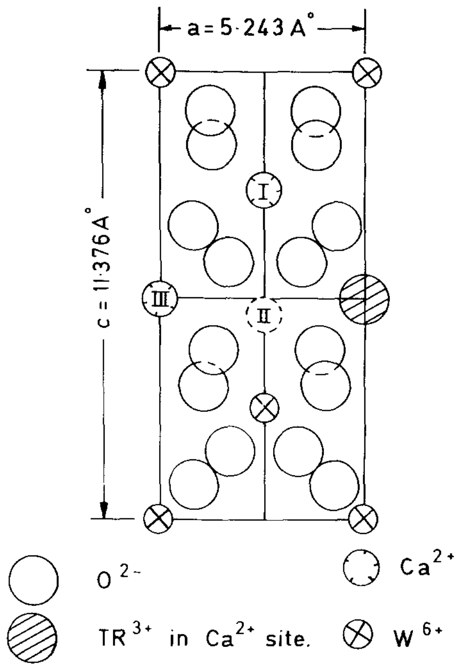

Figure 6 Projection of the $CaWO_4$ unit cell on the a–c plane. Sites I, II and III are possible positions of compensating defects.

ions in W sites as a source for anomalous transitions. In fact, substitution in W sites, whenever it occurs, will give an ESR spectra distinguishable from that due to ions substituting in Ca sites because of the different environment for each site.

(c) A third kind of transition could be identified as weaker transitions corresponding to $\Delta M = \pm 2$ (forbidden transitions). These lines are to be expected whenever b_2^0 is so large as to be comparable with $g\beta H$, as reported by Hempstead and Bowers for Gd^{3+} in $CaWO_4$ [3].

(d) Hyperfine transitions, due to the odd isotopes, if present, having a net nuclear spin I, give a hyperfine spectrum of low intensity compared to the main transitions. Examples of these effects could be demonstrated by the spectra of $Gd^{3+}/CaWO_4$ [3], $Nd^{3+}/CaWO_4$ [16, 20] and $Yb^{3+}/CaWO_4$ [21].

From the above summary, we see that none of the four mentioned causes can be the reason for the extra component reported here. This, therefore, must be classified as having a separate and distinct cause. The only previous work in which a fairly close similarity of behaviour existed was that of Forrester and Hempstead [22], who observed unresolved doublets in the ESR spectra of $Tb^{3+}/CaWO_4$ single crystals. Their observations, as far as splitting is concerned, were as follows. With increase of the angle θ between the applied magnetic field and the c-axis of the crystal, the lines were broadened. At K-band (23 GHz) and a temperature of 4.2 K, the linewidth increased from 1.4 G when $\theta = 0°$, to about 15 G when $\theta = 60°$. The line shape was distorted as θ was further increased, the peaks became somewhat flattened and at angles greater than about 70° the lines became partially resolved into doublets. The highest field transition was better resolved than the lowest field line. Forrester and Hempstead interpreted this behaviour as indicating that two types of Ca site are not completely equivalent. As regards the present results we suggest that some of the Gd^{3+} ions may have slightly defected sites which would not disturb the crystal field symmetry radically in their vicinity, but cause the transitions to shift slightly on the field axis. If we examine the unit cell of $CaWO_4$ (Fig. 7) we see in the (0 0 1) plane, the nearest neighbours to a Ca site an an angle ϕ about 50° are oxygen ions (Farley, Saunders and Chung, [23]). Knowing that the oxygen ions provide the framework of the crystal field symmetry at the Ca site we should expect some change in crystal field due to oxygen vacancies. We propose an ordered oxygen vacancy model to account for the slight difference in Ca^{2+} site symmetry. This model also accounts for the

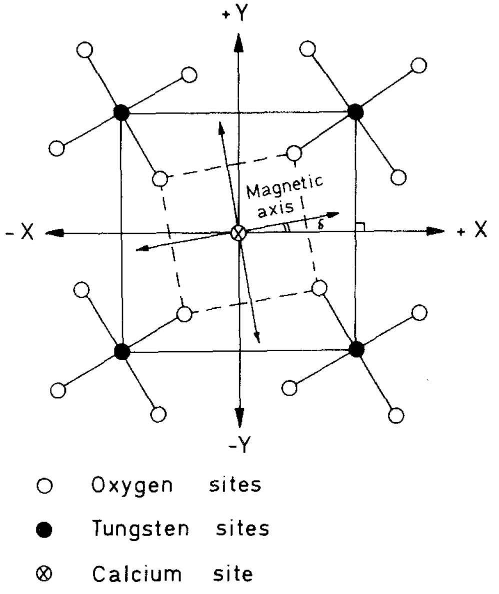

Figure 7 Projection on the (0 0 1) plane of the scheelite unit cell. The conventional + z-axis emerges from the plane of the paper; σ is the angle between the crystal axis and the magnetic axis.

dependence of the intensity of the extra component on temperature. As the temperature is reduced the possibility of these oxygen vacancies settling in an ordered form increases and this leads to a corresponding increase in the intensity of the extra component, which arises from Gd^{3+} ion situated in a Ca^{2+} site having no adjacent oxygen vacancies. Supporting evidence for the ordered oxygen vacancy model can be drawn from the recently reported relaxation time studies on the same material [24]. As already noted the preliminary study showed clearly the existence of two components in the $\Delta M = 1$ transition having slightly different relaxation rates while the later study, in which a T^{-3} dependence in the Raman region was established, showed that a substantial number of defects were present in the crystals.

Acknowledgement

We wish to thank Messrs T. Harcourt and C. Savage for their help in the preparation of oriented specimens. One of us (EAEA) also wishes to thank the University of Alexandria, Egypt, for the award of a Research Scholarship.

References

1. J. S. THORP, H. P. BUCKLEY and G. BROWN, *J. Mater. Sci.* **9** (1974) 864.
2. R. W. G. WYCKOFF, "Crystal Structures", (Interscience, New York, 1948).
3. C. F. HEMPSTEAD and K. D. BOWERS, *Phys. Rev.* **198** (1960) 131.
4. A. ARBEL and R. J. STOKES, *J. Appl. Phys.* **36** (1965) 1460.
5. A. ZALKIN and D. H. TEMPLETON, *J. Chem. Phys.* **50** (1964) 501.
6. H. P. BUCKLEY, Ph.D. Thesis, University of Durham (1973).
7. J. M. FARLEY and G. A. SAUNDERS, *J. Phys. C.* **5** (1972) 3021.
8. J. M. FARLEY, Ph.D. Thesis, University of Durham (1973).
9. B. BLEANEY and K. W. H. STEVENS, *Rep. Prog. Phys.* **16** (1953) 108.
10. V. M. VINOKUROV and V. G. STEPANOV, *Sov. Phys. Sol. State* 9 (1967) 844.
11. A. ABRAGAM and M. H. L. PRYCE, *Proc. Roy. Soc. A* **205** (1951) 135.
12. J. S. M. HARVEY and H. KIEFTE, *Canad. J. Phys.* **49** (1971) 995.
13. V. F. DERNOV-PEGAREV, M. M. ZARIPOV, M. I. SAMOILOVICH and V. G. STEPANOV, *Sov. Phys. Sol. State* 8 (1966) 197.
14. J. S. THORP, G. BROWN and H. P. BUCKLEY, *J. Mater. Sci.* 9 (1974) 1337.
15. K. NASSAU and A. M. BROYER, *J. Appl. Phys.* **33** (1962) 3064.
16. R. W. KEDZIE and M. KESTIGIAN, *Appl. Phys. Lett.* **3** (1963) 86.
17. R. Yu. ABDULSABIROV, A. A. ANTIPIN, I. N. KURKIN, E. A. TSVETKOV, Yu. K. CHIRKIN and V. I. SHLENKIN, *Sov. Phys. Sol. State* **14** (1972) 255.
18. W. B. MIMS and R. GILLEN, *J. Chem. Phys.* **47** (1967) 3518.
19. V. VOLTERA, J. BRONSTEIN and M. ROCKNI, *Appl. Phys. Lett.* 8 (1966) 212.
20. C. G. B. GARRETT and F. R. MERRITT, *ibid.* **4** (1964) 31.
21. V. RANON and V. VOLTERRA, *Phys. Rev.* **134** (1964) A1483.
22. P. A. FORRESTER and C. F. HEMPSTEAD, *ibid.* **126** (1962) 923.
23. J. M. FARLEY, G. A. SAUNDERS and D. Y. CHUNG, *J. Phys. C. (Solid State Phys.)* 8 (1975) 780.
24. J. S. THORP and E. A. E. AMMER, *J. Mater. Sci.* **11** (1976) 1215.

Received 5 May and accepted 6 July 1978.