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Effect of thermochemical reduction on the electrical, optical-absorption, and positron-annihilation characteristics of ZnO crystals

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The electrical properties, optical-absorption characteristics, and positron-annihilation lifetimes have been determined for nominally pure ZnO single crystals that were thermochemically reduced in Zn vapor in the temperature range between 1100 and 1500 K. Electrical-conductivity and Hall-effect measurements indicate that donors are produced as a result of the thermochemical reduction process. Additionally, optical measurements show that the reduction results in an increase in the optical absorption near the two fundamental absorption edges. Positron-annihilation studies reveal that a well-defined positron state having a lifetime of 169±2 ps exists in the reduced crystals, in contrast to the lifetime of 180±3 ps characteristic of colorless, high-resistivity as-grown crystals. The lifetime of 169 ps is attributed to positron annihilation in the bulk material. It is concluded that defects produced by thermochemical reduction of ZnO are not efficient positron traps—indicating that the defects either exist as interstitials or that they are positively charged.

I. INTRODUCTION

Single crystals of ZnO have the wurtzite structure and have a band gap of ~3.2 eV. They are usually semiconducting. Depending on the stoichiometry or the presence of impurities, the resistivity of ZnO can vary widely in the range between 10^{17} and 10^{-3} Ω cm. While ZnO with resistivities in the semiconducting range of 10^2 to 1 Ω cm is commonly produced,[1] stoichiometric ZnO crystals exhibiting a relatively low electrical conductivity can be grown under carefully controlled conditions. In the semiconducting form, ZnO is characterized by interesting optical, thermal, and other properties that make it a promising material for applications in electro-optic and semiconducting devices. Accordingly, the physical and electronic properties of ZnO have been the subject of a number of previous investigations.[1–14]

In addition to extrinsic doping or impurity effects, defects produced by thermal treatment or by irradiation with energetic particles can strongly influence the properties of ZnO. Defects resulting from the thermal treatment of ZnO are of particular interest since their nature remains a subject of controversy in spite of numerous previous studies. It is generally accepted that the thermal treatment of ZnO at elevated temperatures produces a stoichiometric excess of Zn since the vapor pressure of oxygen is greater than that of Zn at high temperatures. Accordingly, in early models of the reduction process, Zn^0 interstitials were proposed as the donor centers responsible for the observed increases in the ZnO electrical conductivity. For example, Mohanty and Azároff[13] performed x-ray-diffraction measurements on thermochemically reduced ZnO crystals and concluded that there were $(1.6-6.0)\times 10^{20}$ Zn^0 interstitials/cm^3. Subsequently, however, Appleton and Feldman[15] used beams of ^{4}He ions in unidirectional Rutherford backscattering (RBS) channeling and blocking experiments to study ZnO samples prepared in the same manner as those investigated by Mohanty and Azároff. Zn^0 interstitials were not detected in the RBS channeling studies, and Appleton and Feldman concluded that if such interstitials were, in fact, present, their concentration would have to be less than 6×10^{18} cm^{-3}. As indicated by these contradictory x-ray and RBS results, the Zn^0 interstitial model is clearly controversial.

Oxygen vacancies or the possible formation of other defects have also been proposed to account for the observed increases in the electrical conductivity of ZnO following thermal treatments.[2–4,9,11,16,17] The oxygen-vacancy model is supported by its ability to provide a consistent interpretation of the electrical transport measurements. In this model, oxygen vacancies are doubly ionized donors, and it is this interpretation that appears to be most compatible with the experimental results for either as-grown or thermochemically reduced ZnO crystals.[9,11,16]

Positron-annihilation spectroscopy (PAS) provides a sensitive method for investigating vacancy-type defects, and it has proven to be useful in determining the nature of intrinsic defects in metals, insulators, and semiconductors.[18,19] As a result of strong Coulombic repulsion by the lattice ions, thermalized positrons move in interstitial regions of the crystal and are characterized by an extended Bloch state. Positrons can annihilate either as these Bloch positrons (i.e., in the free state) or as trapped positrons in a bound state. Among other defects, vacancylike defects act as positron traps if they are neutral or negatively charged. Positively charged defects, on the other hand, are generally not considered to be effective positron traps.[20] It is known that the positron lifetime in the free state τ_b is shorter than in the trapped state τ_v. A crystal containing positron traps generally gives an experimental lifetime spectrum characterized by an average lifetime $\bar{\tau}$ which is related to τ_b and τ_v and to the trapping rate. Accordingly, measurements of the positron lifetimes can provide valuable information regarding the defect structure in a solid.

In the present work, positron-annihilation, electrical-conductivity, Hall-effect, and optical-absorption measurements have been used to investigate changes in the electrical properties of ZnO single crystals following thermochemical reduction treatments in Zn vapor. The purpose of these studies is to investigate the nature of the resulting defects, in order to shed light on the relative merits of the interstitial versus vacancy defect models. Additionally, information on the positron-annihilation parameters is applicable to an evaluation of the recent model for positron screening in semiconductors and insulators proposed by Puska *et al.*[21]

II. EXPERIMENTAL PROCEDURES

Single crystals of ZnO grown using two different techniques and obtained from two different sources were employed in the electrical, optical, and positron-annihilation measurements reported here. Flux-grown ZnO single crystals were obtained from Airtron/Litton Industries, and single crystals were also grown at ORNL using a chemical-vapor-transport technique. The thermochemical reduction (TCR) was carried out in a horizontal furnace with the ZnO samples contained in an evacuated refractory tube along with zinc metal. The reduced samples were rapidly cooled following the thermal treatment. The electron irradiation was carried out using electrons from a 2.0-MeV Van de Graaff accelerator (High Voltage Engineering).

Electrical-conductivity and Hall-effect measurements were made on samples having dimensions of about $1.0\times1.0\times0.1$ cm^3 using electrical contacts in the van der Paw configuration. The near-infrared, visible, and ultraviolet (ir-vis-uv) measurements were made using a Perkin-Elmer Lambda 9 spectrophotometer. Infrared spectra were obtained by using a Perkin-Elmer model 983G spectrophotometer. Samples consisting of pairs of single-crystal plates were employed in the positron-annihilation measurements. A ^{22}NaCl positron source ($\sim$0.5 MBq) enclosed in a 0.4 mg/cm^2 Ni foil was sandwiched between two sample plates, and the positron lifetime spectra were obtained using a fast-fast coincidence system with a resolution of 300 ps [full width at half maximum (FWHM)].

III. RESULTS AND DISCUSSION

Both the electrical and optical properties of the thermochemically reduced ZnO were strongly altered following thermochemical reduction treatments as indicated by the following results.

A. Electrical-conductivity and Hall-effect measurements

The flux-grown ZnO single crystals obtained for Airtron/Litton were characterized by relatively low electrical conductivity. Following TCR, however, these samples became semiconducting. Hall measurements showed that the carriers were donors. It is clear that these donors were thermally generated during TCR. The concentration of donors, as determined from $(Re)^{-1}$ where R is the Hall coefficient, was found to increase with the TCR temperature as illustrated in Fig. 1. The concomitant increase in the electrical conductivity is shown in Fig. 2. The Hall mobility was determined to be in the range of 110–130 cm^{2}V^{-1}s^{-1}. While no attempt was made to determine an activation energy from the results (since the Zn vapor pressure was not a constant), the data in Figs. 1 and 2 clearly illustrate the monotonic dependence of the donor concentration and the electrical conductivity on the TCR temperature.

B. Optical-absorption measurements

The optical-absorption spectra obtained in the ir-vis-uv regions (i.e., for photon energies above 0.5 eV) for three ZnO samples are shown in Fig. 3. Infrared absorption results (i.e., for photon energies below 0.6 eV) for the same three samples are illustrated in Fig. 4. The spectrum labeled *a* in the figures was obtained using an as-grown single crystal with low electrical conductivity. Between 3.0 and 0.1 eV the optical absorption was relatively low and constant as shown in Figs. 3 and 4. After TCR at a temperature of 1273 K, however, the regime in which the optical absorption was low was significantly reduced as shown in the spectrum labeled *b* in Fig. 3 and was confined to between 2.0 and 1.0 eV. Outside of this range, the absorption became relatively intense. The far-

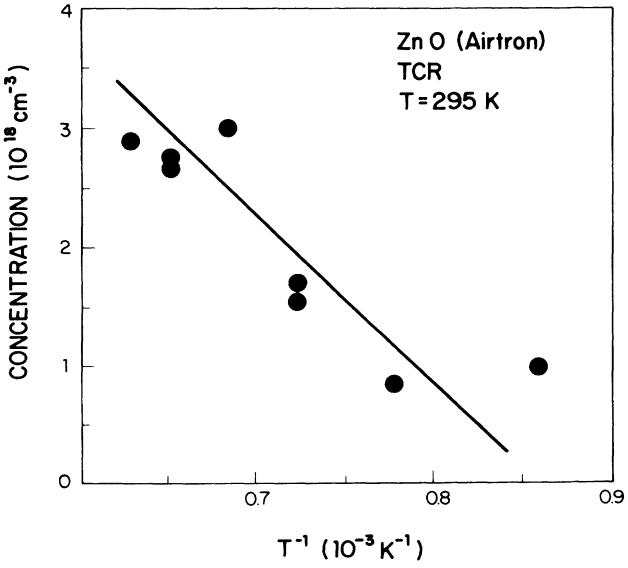

FIG. 1. Donor concentration vs T^{-1} following TCR in Zn vapor at elevated temperatures.

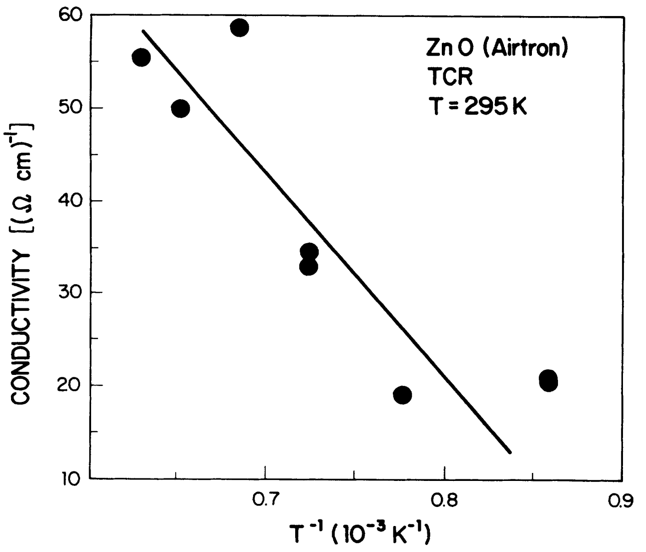

FIG. 2. Conductivity vs T^{-1} following TCR in vapor at elevated temperatures.

TABLE I. Positron lifetime in as-grown Airtron/Litton ZnO crystals and after TCR for 2 h.

Pairs	TCR (K)	Positron lifetime (ps)
1	as grown	182±3
2	1163	169±2
3	1273	170±1
4	1537	169±4
5	1590	169±2

infrared "tail" of the absorption spectrum is illustrated in curve *b* of Fig. 4. Following TCR of ZnO at the higher temperature of 1537 K, the absorption at the two sides of the spectrum became even more pronounced as illustrated in curves *c* in Figs. 3 and 4. The spectra show, in fact, that some increase in optical absorption occurs in all regions of the spectrum following the TCR treatments. The ZnO crystals became visibly brownish in color as a result of the reduction process, and this coloration increased in intensity as the TCR temperature was raised. The three samples in Figs. 3 and 4 correspond to the sample pairs numbered 1, 3, and 4 in Table I, and a comparison of the results clearly shows that the observed increase in the optical absorption coincides with an increase in the ZnO electrical conductivity.

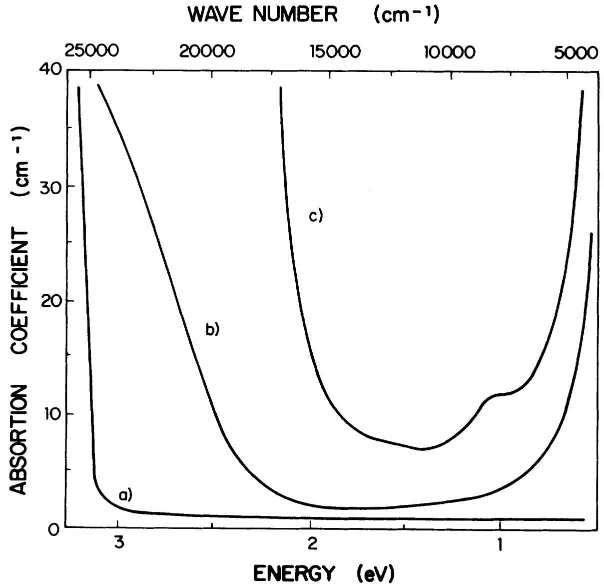

FIG. 3. uv, visible, and near-infrared absorption spectra for curve *a*, as-grown pair 1; curve *b*, pair 3 after TCR at 1273 K; curve *c*, pair 4 after TCR at 1537 K.

C. Positron-annihilation measurements

The positron-lifetime spectra with 1×10^6 counts were analyzed by means of the program POSITRONFIT EXTENDED.[22] Two source corrections were made to take into account the positron annihilation in the positron source. These corrections were obtained from analyses of the lifetime spectra of several reference samples.

The positron-lifetime spectrum in a crystal arises from the addition of different exponential terms. Each of these exponential terms corresponds to a different annihilation mode of the positrons in the crystal. Thus the number of components in the spectrum might give, in principle, the

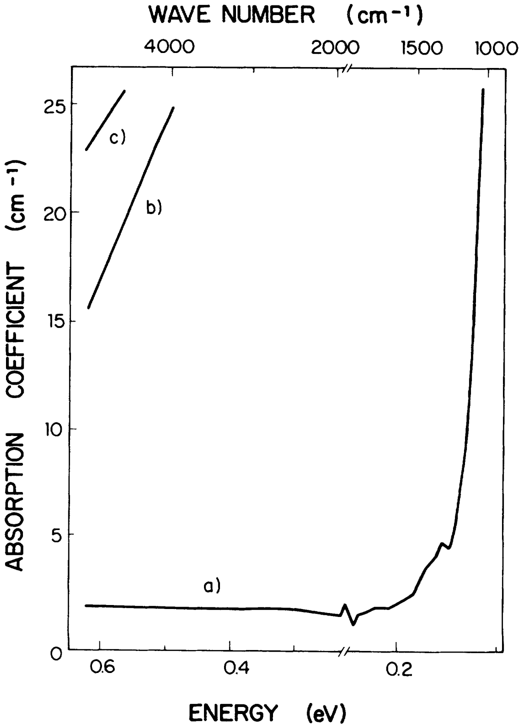

FIG. 4. ir absorption spectra. Curve *a*, as-grown pair 1; curve *b*, pair 3 after TCR at 1273 K; curve *c*, pair 4 after TCR at 1537 K.

number of states in which the positrons annihilate in the crystal. An exponential component is characterized by its corresponding decay rate, $\lambda_i = \tau_i^{-1}$. So, a two-component spectrum is due to positrons annihilating in two different states which may be characterized by the corresponding decay rate λ_i. When a spectrum is "single component" it is accepted that either almost all positrons annihilate in a single state or, if there is more than one state, their decay rates are so close that there is no possibility of separating the different components.

All of the lifetime spectra were well fit by using a single exponential term, and two-component fits yielded either unacceptable variances or unreasonable parameters. The positron lifetimes τ obtained from the decay rate of the single exponent terms are summarized in Table I, and the results indicate that the lifetime decreases with increasing donor concentration (see Fig. 5). The results for the as-grown material (pair 1) yield a lifetime of 182±3 ps. Following the TCR treatment, however, a shorter lifetime of about 169 ps was obtained for all of the samples independent of the TCR temperature. Since the minimum observed lifetime was 169 ps, we attribute this lifetime to positron annihilation in the free state (also called the bulk positron lifetime τ_b). This value is in the expected range for positron annihilation in the bulk. [In MgO τ_b(expt.) = 166 ps; τ_b(theor.) = 167 ps.]

The τ_b value was observed either after the crystals were annealed in oxygen or after TCR, indicating that the defects present in the crystal after the thermal treatments are not effectively positron traps. This means these defects should be either (1) positively charged vacancies (since if they were neutral or negatively charged they should trap positrons), or (2) interstitials since it is known that positrons are insensitive to interstitials. (In MgO the lifetime of a positron trapped in F-type or V-type defects is $\tau_v \sim 200$ ps.)

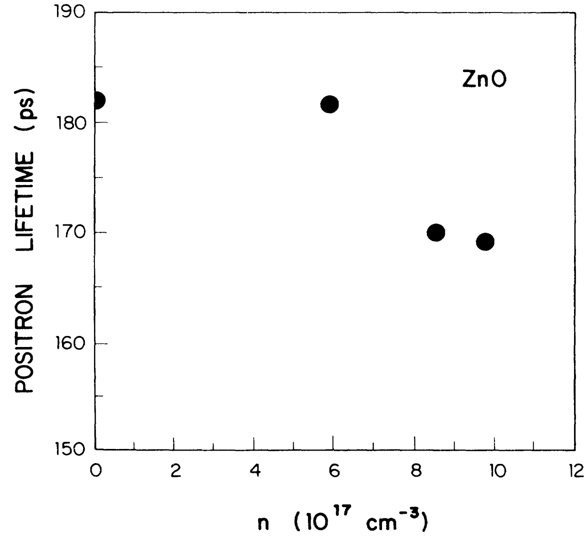

FIG. 5. Positron lifetime against donor concentration. The data point at $n = 6\times10^{17}$ cm^{-3} corresponds to a sample electron irradiated with a cumulative dose of 1.3×10^{18} e^- cm^{-2} (the energy of the electrons was 1.8 MeV).

In general, TCR in oxides produces F centers (i.e., in this case, oxygen vacancies each having two electrons so that the defect is electrically neutral with respect to the lattice). For the cases of MgO and CaO, however, it has recently been observed that the removal of protons either before or during TCR results in the production of anion vacancies that are primarily in the one-electron F^+ state (i.e., positively charged with respect to the lattice).[23] If ZnO were to behave in a similar manner, the presence of hydrogen in the crystals would increase the F and F^+ concentrations following TCR.

D. Heat treatments in other environments

The results described in Secs. III A–III C above for flux-grown Airtron/Litton ZnO crystals have been compared with the results obtained for crystals grown by the chemical-vapor-transport technique. Additionally, the optical-absorption and PAS studies have been extended to include crystals that were heat treated in other environments, and in particular, ZnO specimens were investigated following heat treatments in oxygen or nitrogen. The crystals heated in nitrogen gas were placed in a graphite container in order to assure an oxygen-free environment.

It was found that heat treatments in Zn vapor, nitrogen, and oxygen all produced the same basic trend in the optical-absorption and positron-annihilation characteristics. The observed rate of change, however, was different for the different environments with the fastest rate of change observed for treatment in Zn vapor—followed by treatment in nitrogen gas, and finally heating in oxygen. As noted earlier, the vapor pressure of oxygen at elevated temperatures is greater than that of zinc, and therefore, even in an oxygen atmosphere ZnO experiences some TCR at high temperatures.

One pair of ZnO crystals from Airtron/Litton and two pairs of chemical-vapor-transport grown crystals from ORNL were annealed at progressively higher temperatures (see Table II). While all of the samples exhibiting a decay constant of about 169 ps also showed a noticeable increase in optical absorption near the two fundamental edges, once the lifetime has decreased to 169 ps, further heat treatment at increasing temperatures did not result in a change in this value.

The as-grown single crystals that did not exhibit any visible coloration were characterized by a lifetime of ~180 ps as previously noted (e.g., see the results for pairs 1, 7, and 8). For pair 6, which exhibited a slightly green color, however, the positron lifetime for the as-grown state was relatively high, i.e., 203±3 ps. The fact that the positron lifetime in the as-grown, uncolored samples is the same, independent of the origin of the samples, suggests that the lifetime value of ~180 ps corresponds to an average value between the positron lifetime in the bulk and in a state localized at some common intrinsic defect. The lifetime of ~180 ps cannot be attributed to positron annihilation at an oxygen defect since the ZnO experiences a TCR process even when the crystals are annealed

TABLE II. Positron lifetime in as-grown ZnO crystals and after successive oxidizing or reducing treatments for 60 min.

		Treatment		
Pair no.	Source	Nitrogen T (K)	Oxygen T (K)	Positron lifetime (ps)
6	Airtron/Litton	as grown		203±3
			1273	178±1
			1473	175±1
		1273		177±1
		1473		173±1
7	ORNL	as grown		181±1
		873		181±1
		973		180±1
		1073		169±1
		1173		169±1
		1273		168±1
		1373		169±1
		1473		169±1
8	ORNL		as grown	179±1
			873	178±1
			973	174±1
			1073	171±1
			1173	171±1
			1273	171±1
			1373	171±1
			1473	173±1

in oxygen. Thus, after annealing, regardless of the atmosphere, this oxygen defect concentration should be higher, but the observed lifetimes decrease approaching 169 ps. The longer lifetime of 203 ps observed for the slightly green-colored sample (pair 6) is likely to correspond to the positron lifetime in some trapped state arising from defects associated with the incorporation of an impurity. It should be noted that the ratio of the lifetimes $\frac{203}{169}=1.2$ is close to the ratio between the lifetime of vacancy-trapped positrons and the bulk lifetime observed previously in some semiconductors[18–20] and simple oxides.[24,25] Finally, the value of 169 ps associated with the positron lifetime in the bulk of ZnO following TCR is in better agreement with the predictions of the insulator model than with those of the semiconductor model—both models being previously proposed by Puska *et al.*[21] (see Fig. 3 in Ref. 21).

IV. SUMMARY AND CONCLUSIONS

In nominally pure ZnO single crystals, electrical-conductivity and Hall-effect measurements indicate that donors are produced as a result of thermochemical reduction. The concentration of these donors increases with increasing temperature of the TCR treatment. The Hall mobility was determined to be approximately 120 cm^2 V^{-1} s^{-1}.

Optical-absorption spectra show that, regardless of the annealing atmosphere, the absorption increases near two fundamental edges that are observed following thermochemical treatment. This increase is most pronounced if the heat treatment is carried out in Zn vapor, and smaller effects are observed when the samples are treated in an oxygen atmosphere.

Positron-annihilation measurements made after TCR reveal a well-defined positron state in ZnO whose lifetime is 169±2 ps. This state is attributed to free positron annihilation in the bulk material. Positron-annihilation spectra have also been observed with a lifetime of ~180 ps in as-grown colorless crystals and with a lifetime of 203 ps in as-grown crystals that exhibited a slight green coloration. The higher value of 203 ps may represent the lower value for the positron lifetime in some vacancy-type defect. In either case, as a result of thermochemical reduction, the positron lifetime was decreased to 169 ps and the as-grown defects were rendered ineffective as positron traps. Those defects created by thermochemical reduction (i.e., the defects associated with the appearance of the optical-absorption increases near the two band edges) are apparently not effective positron traps, and therefore should either be positively charged defects such as the F^+ center or interstitials. Since the work of Appleton and Feldman[15] has set an apparent limit on the interstitial concentration, the presence of positively charged defects seems to offer the more likely explanation.

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[1] D. G. Thomas and J. J. Lander, J. Chem. Phys. **25**, 1136 (1956).

[2] S. E. Harrison, Phys. Rev. **93**, 52 (1954).

[3] A. R. Hutson, Phys. Rev. **108**, 222 (1957).

[4] D. G. Thomas, J. Phys. Chem. Solids **3**, 229 (1957).

[5] G. Heiland, E. Mollwo, and F. Stöckmann, in *Solid State Physics: Advances in Research and Applications,* edited by F. Seitz and D. Turnbull (Academic, New York, 1959), Vol. 8, p. 191.

[6] W. E. Vehse, W. A. Sibley, F. J. Keller, and Y. Chen, Phys. Rev. **167**, 828 (1968).

[7] J. M. Smith and W. E. Vehse, Phys. Lett. **31A**, 147 (1970).

[8] C. González, D. Galland, and A. Herve, Phys. Status Solidi B **72**, 309 (1975).

[9] B. Utsch and A. Hausmann, Z. Phys. B **21**, 27 (1975).

[10] K. I. Hagemark and L. C. Chacka, J. Solid State Chem. **15**, 261 (1975).

[11] E. Ziegler, A. Heinrich, H. Oppermann, and G. Stöver, Phys. Status Solidi A **66**, 635 (1981).

[12] G. D. Mahan, J. Appl. Phys. **54**, 3825 (1983).

[13] G. P. Mohanty and L. V. Azároff, J. Chem. Phys. **35**, 1268 (1961).

[14] M. Nitzau and Z. Burshtein, Phys. Status Solidi A **58**, K141 (1980).

[15] B. R. Appleton and L. C. Feldman, J. Phys. Chem. Solids **33**, 507 (1972).

[16] A. Hausmann and B. Utsch, Z. Phys. B **21**, 217 (1975).

[17] K. I. Hagemark, J. Solid State Chem. **16**, 293 (1976).

[18] G. Dlubek and R. Krause, Phys. Status Solidi A **102**, 443 (1987).

[19] C. Corbel, M. Stucky, P. Hautojärvi, K. Saarinen, and P. Moser, Phys. Rev. B **38**, 8192 (1988).

[20] M. J. Puska, O. Jepsen, O. Gunnarsson, and R. M. Nieminen, Phys. Rev. B **34**, 2695 (1986).

[21] M. J. Puska, S. Mäkinen, M. Manninen, and R. M. Nieminen, Phys. Rev. B **39**, 7666 (1989).

[22] P. Kirkegaard and M. Eldrup, Comput. Phys. Commun. **7**, 401 (1974).

[23] Y. Chen, V. M. Orera, R. González, R. T. Williams, G. P. Williams, G. H. Rosenblatt, and G. J. Pogatshnik, Phys. Rev. B **42**, 1410 (1990).

[24] M. A. Pedrosa, R. Pareja, R. González, and M. M. Abraham, J. Appl. Phys. **62**, 429 (1987).

[25] M. Forster, J. N. Mundy, and H. E. Schaefer, in *Positron Annihilation,* edited by L. Dorikens-Vanpraet, M. Dorikens, and D. Segers (World Scientific, Singapore, 1989), p. 833.