

phys. stat. sol. (b) 122, 175 (1984)

Subject classification: 13.4 and 13.5.3; 14.3; 19; 22.6.1

Laboratoire de Spectrochimie du Solide, Université Pierre et Marie Curie, Paris¹) (a)
and Département de Chimie, Université Cadi Ayyad, Marrakech (b)

Small Polaron Mobility in α - $\text{Li}_x\text{V}_2\text{O}_5$

By

C. SANCHEZ (a), M. HENRY (a), R. MORINEAU (a), and M. C. LEROY (b)

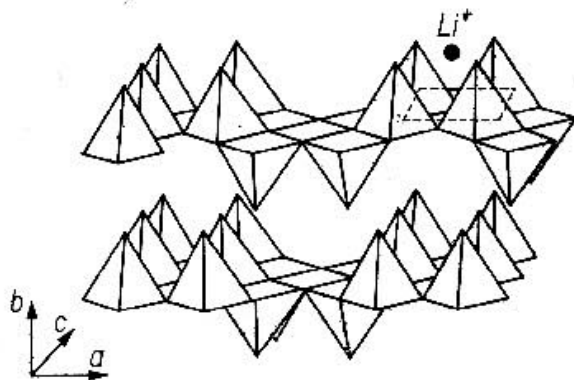
ESR and dc conductivity measurements are performed on a $\text{Li}_x\text{V}_2\text{O}_5$ ($x = 0.001$) single crystal in the temperature range 4 to 293 K. They suggest that at low temperature, the unpaired electron remains localized in the field of lithium ion and is equally delocalized over four vanadium sites leading to the formation of a bound polaron characterized by a 29 hyperfine lines ESR spectrum. As the temperature is raised bound polarons are freed from the electrostatic field and the electrical properties of the sample above 250 K mainly arise from the hopping of free polarons between the vanadium sites. A comparison with previous measurements on non-stoichiometric V_2O_5 shows that the activation energy corresponding to the hopping process of free polarons does not depend on the nature of the paramagnetic defect, but it appears that the energy needed to extract the bound polaron from the Coulomb field of the defect decreases when the overall radius of the defect increases.

EPR und Messungen der Gleichstromleitfähigkeit werden an einem $\text{Li}_x\text{V}_2\text{O}_5$ ($x = 0,001$)-Einkristall im Temperaturbereich 4 bis 293 K durchgeführt. Sie zeigen, daß bei tiefen Temperaturen das ungepaarte Elektron lokalisiert bleibt im Feld des Lithiumions und gleichförmig delokalisiert ist über vier Vanadiumplätze, was zu der Bildung eines gebundenen Polarons führt, das durch ein EPR-Spektrum mit 29 Hyperfeinlinien charakterisiert ist. Bei Temperaturerhöhung werden die gebundenen Polaronen aus dem elektrostatischen Feld befreit und die elektrischen Eigenschaften der Probe oberhalb 250 K rühren hauptsächlich vom Hopping-Mechanismus der freien Polaronen zwischen den Vanadiumplätzen her. Ein Vergleich mit früheren Messungen an nichtstöchiometrischem V_2O_5 zeigt, daß die dem Hoppingprozeß freier Polaronen entsprechende Aktivierungsenergie nicht von der Art des paramagnetischen Defekts abhängt, sondern es scheint, daß die Energie, die zur Befreiung des gebundenen Polarons aus dem Coulombfeld des Defekts notwendig ist, abnimmt, wenn der Gesamtradius des Defekts wächst.

1. Introduction

Stoichiometric vanadium pentoxide V_2O_5 should be a diamagnetic insulator with a band gap of 2.3 eV [1]. It is however possible to produce a non-stoichiometric oxide containing a non-integer number of d-electrons per vanadium. These unpaired electrons can be introduced by oxygen deficiency, vanadium substitution by an hexavalent ion (W^{6+} , Mo^{6+}), or insertion of a monovalent ion such as Li^+ [2]. At low temperature, the unpaired d-electrons remain trapped in the Coulomb field due to the defect. Depending on the nature of the doping impurity, the extra electron may be localized on a single vanadium site ($\text{W}_x\text{V}_2\text{O}_5$) or delocalized among two (non-stoichiometric V_2O_5) or even four vanadium sites ($\text{Li}_x\text{V}_2\text{O}_5$). At higher temperature, an electron hopping between vanadium ions in different valence states [3, 4] is observed giving rise to the semiconducting properties [5 to 7]. A strong electron-phonon coupling occurs in the vanadium oxide, leading to the formation of small polarons. The charge carriers are then small polarons. Vanadium oxide is then a low-mobility n-type semiconductor [6] and its semiconducting properties are usually described by the small polaron hopping model suggested by Mott.

¹) 4 place Jussieu, T. 44, 75230 Paris Cédex 05, France.

Fig. 1. Nature of the defect in $\text{Li}_x\text{V}_2\text{O}_5$.

ESR and dc conductivity experiments have recently been performed on non-stoichiometric V_2O_5 single crystal [8]. They suggest the presence of free and bound polarons. At low temperature, the unpaired electron remains localized on two vanadium sites associated with an oxygen vacancy leading to the formation of a so-called "bound polaron". Only direct hopping between localized states can occur and the electrical conductivity is quite low. At higher temperature, the thermal energy kT becomes large enough to extract the unpaired electron from the electrostatic field of the oxygen vacancy and the electrical properties mainly arise from the hopping of "free polarons" between vanadium sites that are not associated with the defect. It is well known that the nature of the paramagnetic defect can be deeply modified by adding foreign impurities. Lithium ions, for instance, can be inserted along the channels of the orthorhombic V_2O_5 lattice (Fig. 1). At low temperature, the unpaired electron remains associated with this positive extra-charge and appears to be delocalized over the four equivalent vanadium sites surrounding the Li^+ ion [9]. As in non-stoichiometric V_2O_5 a hopping process of the small polaron is observed at higher temperature. A study of this hopping process will be described in this paper. ESR and dc conductivity measurements will be performed on the same single crystal in order to allow a straightforward comparison between both kinds of results. We shall show that the free-and bound-polaron model can account for the experimental results. A comparison will be made with previous results on non-stoichiometric V_2O_5 .

2. Experimental

$\text{Li}_x\text{V}_2\text{O}_5$ single crystals were produced by slow cooling from the melt of a mixture of vanadium pentoxide (Johnson-Matthey Specpur) and lithium carbonate in the stoichiometric ratio. The lithium concentration in the $\text{Li}_x\text{V}_2\text{O}_5$ crystals was checked by atomic absorption ($x = 0.001$). Small dark crystals of about $0.4 \times 0.1 \times 0.2 \text{ mm}^3$ were obtained and easily cleaved along the ac plane of the V_2O_5 structure [10]. X-ray powder diffraction experiments were performed on a Philips diffractometer with NaCl as an internal standard. The Debye-Scherrer powder spectrum performed on $\text{Li}_x\text{V}_2\text{O}_5$ is quite the same as for crystalline V_2O_5 suggesting that our crystals correspond to the α -phase of $\text{Li}_x\text{V}_2\text{O}_5$ bronzes in which the basic orthorhombic structure of V_2O_5 is conserved. ESR spectra were recorded on a JEOL ME 3X X-band spectrometer. A goniometric device was used in order to rotate the crystals in the magnetic field. Variable temperature experiments were performed in the range 293 to 4 K with a helium gas cooled Oxford Instruments cryostat. The magnetic field was measured with an NMR proton probe and the microwave frequency with a wavemeter giving an accuracy of $\pm 1 \text{ MHz}$.

dc electrical conductivity was measured along the c -axis of the crystal by a four-probe technique, using two current leads and two potential leads. Electrical contacts

were made with indium soldering. Low-temperature measurements down to 77 K were made in a cryostat cooled with nitrogen gas. Resistance measurements were carried out using a 225 Keithley current source and a 610 C Keithley electrometer.

3. Results

3.1 ESR

Fig. 2 shows the ESR spectra recorded at 4 K on a V_2O_5 single crystal doped with 1 mol $^{0}/_{00}$ Li. 29 well resolved hyperfine lines are observed when the magnetic field is parallel to the crystallographic b -axis (Fig. 2a). A single broad line, about 100 G wide, is observed when the magnetic field lies in the ac plane (Fig. 2b). No detectable variation occurs when the magnetic field rotates around the b -axis, in the ac plane. The 29 hyperfine line spectrum is typical of an unpaired electron equally delocalized over four vanadium sites [9, 11]. It can be described with the following spin-Hamilton-

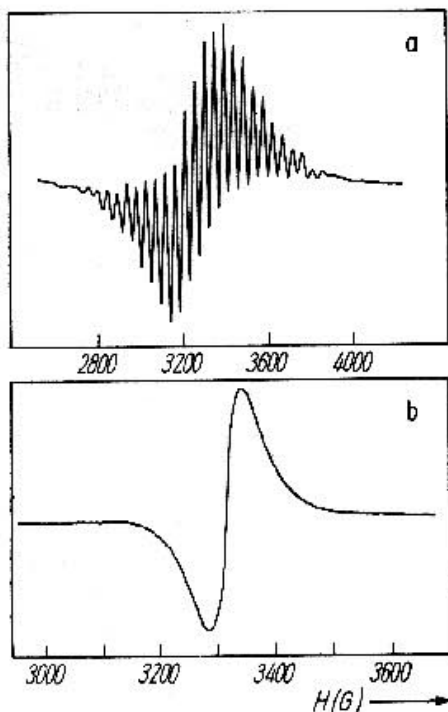


Fig. 2

Fig. 2. ESR spectra of α - $\text{Li}_x\text{V}_2\text{O}_5$ recorded at 4 K. a) $H \parallel b$, b) $H \perp b$

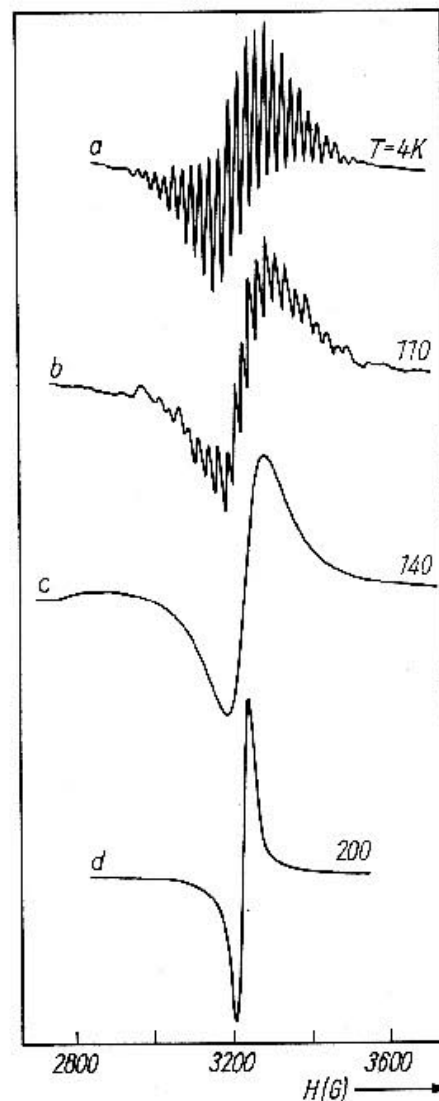


Fig. 3

Fig. 3. ESR spectra of α - $\text{Li}_x\text{V}_2\text{O}_5$ at different temperatures

ian:

$$\mathcal{H} = g_{\parallel} H_z S_z + g_{\perp} (H_x S_x + H_y S_y) + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y),$$

where z , the main axis of the axially symmetric g - and A -tensors, is taken along the b -axis. S and I are the electron ($S = \frac{1}{2}$) and the total nuclear spin ($I = \frac{7}{2} \cdot 4$), respectively.

Calculations, taking into account second-order effects, give

$$g_{\parallel} = 1.912 \pm 0.002, \quad A_{\parallel} = (44.0 \pm 0.5) \text{ G},$$

$$g_{\perp} = 1.981, \quad A_{\perp} = 17 \text{ G (estimated)}.$$

The g -values are very close to those of α - $\text{Li}_x\text{V}_2\text{O}_5$ bronzes [11]. The concentration of the paramagnetic centres was determined by double integration of the ESR signal and indicates 10^{-4} unpaired electron per vanadium atom. This result agrees with the observation of a resolved hyperfine spectrum [11, 12].

The ESR spectrum remains well resolved in the parallel direction ($\mathbf{H} \parallel \mathbf{b}$) up to 100 K. The lineshape is Gaussian and the peak-to-peak linewidth is of about 20 G (Fig. 3, curve a). A broadening of the 29 hyperfine lines occurs above 100 K. At 110 K, the lines begin to overlap (Fig. 3, curve b) and a single broad line about 110 G wide is observed at 140 K (Fig. 3, curve c). Its width then decreases with temperature up to 210 K. The lineshape is Lorentzian and the peak-to-peak linewidth is $\Delta H = 38$ G at 200 K (Fig. 3, curve d). Above 210 K a line broadening is again observed.

The ESR spectrum, in the perpendicular direction ($\mathbf{H} \perp \mathbf{b}$) is not resolved at 4 K, no variation is observed up to 77 K. Above this temperature the peak-to-peak linewidth decreases from 60 G at 77 K down to 13 G at 130 K. Above 130 K a line broadening occurs with $\Delta H = 100$ G at 210 K. A plot of the perpendicular linewidth variation versus temperature is shown in Fig. 4. It shows that in the temperature range where a single line is observed, two phenomena occur giving rise to a minimum around 140 K. The first one leads to a narrowing of the signal. It mainly occurs at low temperature. The second one leads to a broadening of the signal and becomes predominant at high temperature.

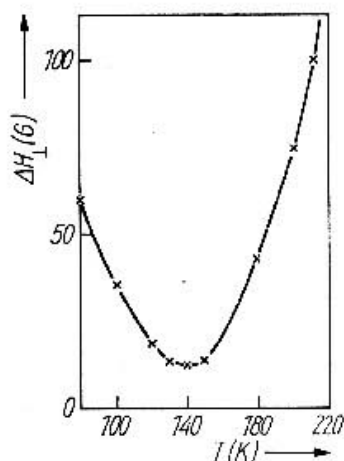


Fig. 4

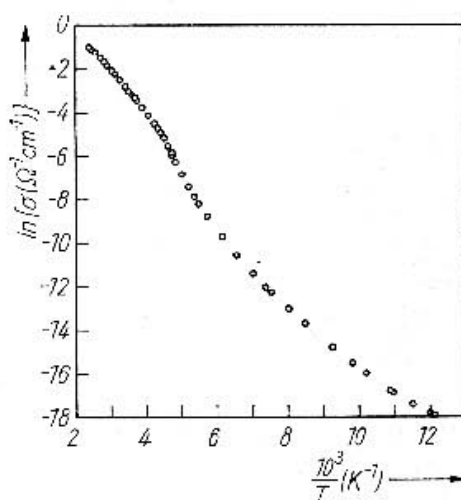


Fig. 5

Fig. 4. Plot of the perpendicular linewidth variation vs. temperature

Fig. 5. Plot of $\ln \sigma$ vs. T^{-1} for α - $\text{Li}_x\text{V}_2\text{O}_5$ crystal along the b -axis

3.2 Electrical conductivity

The dc electrical conductivity of the $\text{Li}_x\text{V}_2\text{O}_5$ ($x = 0.001$) single crystal was measured along the c -direction in the temperature range 77 to 420 K. The crystal used for these experiments was the same as that for ESR. The spin concentration, as measured by double integration of the ESR spectrum at 300 K, corresponds to 2×10^{18} spins/cm³. The room temperature conductivity was $\sigma = 5.8 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$, leading to a mobility of the charge carriers of about $1.8 \times 10^{-1} \text{V}^{-1} \text{s}^{-1} \text{cm}^2$. This value agrees with those previously published in the literature [5, 13, 14]. Fig. 5 shows a plot of $\ln \sigma$ versus T^{-1} . As for V_2O_5 , the conductivity does not follow an exponential law. Between 150 and 225 K the curve is almost linear and the slope is maximum. Above and below these temperatures a curvature is observed and the slope slowly decreases.

4. Discussion

4.1 ESR

Fig. 4 shows that the coalescence of the hyperfine lines cannot be attributed to a temperature-dependent increase of the linewidth only. Two different processes must occur and spin-lattice relaxation processes alone cannot account for experimental observations. The temperature dependence of the ESR linewidth is interpreted according to the random frequency modulation model [15] taking into account two different frequencies. The first one, ν , corresponds to a modulation of the hyperfine interaction by the electron hopping. When the spin-lattice relaxation time is long compared with the hopping frequency, the hopping becomes identical to direct impurity hopping [16]. A lifetime broadening is observed when ν is smaller than the hyperfine parameter A , followed by a motional narrowing when ν becomes larger than A . This process can be mainly seen at low temperature ($100 \text{ K} < T < 200 \text{ K}$). The second frequency, Ω , leads to a continuous broadening, which corresponds to the transition of the unpaired electron toward an excited state with a possible direct spin-lattice relaxation rate [17]. This process becomes predominant at high temperature ($T > 300 \text{ K}$).

Following our previous paper [8], the absorption spectrum is given by

$$I(\omega) = -\text{Re} (W |A^{-1}| \mathbf{I}), \quad (1)$$

where \mathbf{I} is the unit vector and W a vector whose components are the absorption intensities of the 29 individual hyperfine lines. $|A|$ is a complex matrix describing the hopping process. The imaginary part of $|A|$ is a diagonal matrix whose eigenvalues are $\omega - \omega_k$, where ω is the frequency of the magnetic field and ω_k one of the 29 resonance frequencies. The real part includes the different hopping terms and the intrinsic linewidth δ when no hopping occurs. Equation (1) can thus be written [17]

$$I(\omega) = -\text{Re} \left\{ \sum_{k=1}^{29} W_k [i(\omega - \omega_k) - \nu(T) - \Omega(T) - \delta]^{-1} + \nu(T) \right\}^{-1}$$

from which the temperature dependence of $\nu(T)$ and $\Omega(T)$ can be deduced. The ESR spectra were thus simulated by working out the derivative $dI/d\omega$ at each temperature, leading to the determination of the two frequencies ν and Ω . The best fit with an exponential temperature dependence of these two frequencies leads to

$$\nu = \nu_0 \exp \left(-\frac{E}{kT} \right); \quad \nu_0 = 3 \times 10^{11} \text{ Hz}, \quad E = (0.075 \pm 0.005) \text{ eV},$$

$$\Omega = \Omega_0 \exp \left(-\frac{W}{kT} \right); \quad \Omega_0 = 3 \times 10^{10} \text{ Hz}, \quad W = (0.21 \pm 0.02) \text{ eV}.$$

4.2 dc conductivity

In pure V_2O_5 single crystals, Scott et al. [6] attributed the decrease of the activation energies above 370 K to a depletion of the donor centres. This hypothesis was based on several observations:

1. The conductivity appears to be proportional to the number of paramagnetic centres above room temperature, but this relation is no more valid below 300 K [13].
2. The thermoelectric power varies very weakly with temperature above 300 to 350 K indicating that the carrier density remains constant [13, 18].
3. The sign of the Seebeck coefficient indicates a predominantly n-type conduction [14, 18, 13], but a maximum is observed around room temperature [13, 14, 19] suggesting that different conduction mechanisms should occur.

ESR experiments show that at low temperature all unpaired electrons are trapped on localized vanadium sites surrounding Li^+ ions (bound polarons); this was checked by several authors [20, 12] and is typical of interstitial defects (Li^+ , Na^+ , Ag^+ , Cu^+). It is nevertheless feasible that at high temperature these electrons have been freed and the conduction is only due to small polarons hopping between vanadium sites that are not associated with Li^+ impurities (free polarons). At high temperature (above 250 K) a thermally activated mobility of the charge carriers typical of small polaron conduction is observed [13]. In the non-adiabatic regime the conductivity would be given by the following equation [21]:

$$\sigma = \sigma_0 T^{-3/2} \exp\left(-\frac{W}{kT}\right).$$

A plot of $\ln(\sigma T^{3/2})$ versus T^{-1} above 250 K is drawn in Fig. 6, showing that in this temperature range the small polaron model can apply. The high-temperature activation energy deduced from the slope of this curve is $W = (0.21 \pm 0.01)$ eV. This value is in agreement with those measured in non-stoichiometric V_2O_5 [8], and this suggests that the hopping of free polarons is typically independent of the nature of the defect.

An increase of measured activation energy is observed below 225 K. Ioffe and Patrino mentioned that conductivity remains no longer proportional to the number of paramagnetic centres determined by ESR [13]. This suggests that some unpaired electrons remain trapped around the Coulombic field created by Li^+ impurities and therefore do not contribute to conductivity. In this temperature range, conductivity is governed by a two-level hopping system [22], in which mobility μ and the number

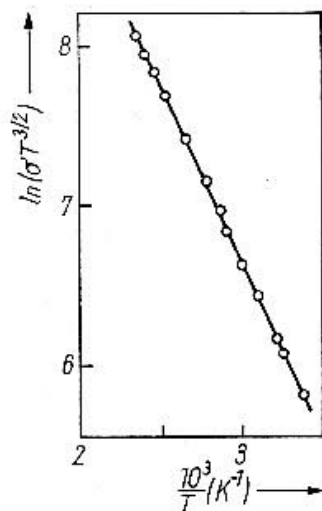


Fig. 6. Temperature dependence of $\ln(\sigma T^{3/2})$ above 250 K of α - $Li_xV_2O_5$ single crystal along the b -axis

of carriers n are both activated. This leads to an increase of the activation energy for conductivity $\sigma = n\mu e$. A comparison between the activation energies observed above and below 225 K in Fig. 5 could give a rough estimate of the energy needed to extract the charge carriers (ionization of localized defects). It is $E \approx 0.08$ eV, this value is roughly in the range of a calculated value [13], but it is smaller than the value measured on pure V_2O_5 crystals [8] (0.10 to 0.12 eV). This suggests that polarons are less bound to the Li^+ impurities than to oxygen vacancies.

According to the small polaron model [23], the observed activation energy should begin to decrease below $\theta_D/2$, such a decrease is actually observed in Fig. 5, below 150 K. This would lead to a Debye temperature of about 300 K ($\hbar\omega_0 \approx 0.027$ eV) a value in close agreement with previous results on V_2O_5 - P_2O_5 glasses [24] and V_2O_5 gels [25, 26], i.e. the electron-phonon coupling defined as $W_p/\hbar\omega_0 \approx 15$ is then quite strong. At low temperature, below 150 K, a decrease of the activation energy down to 0.09 eV is again observed. This value is close to the energy required for the ionization of the defect. It seems reasonable to think that at low temperature unpaired electrons are strongly trapped around lithium ions (as shown by ESR) and that conductivity only arises from direct hopping of bound polarons between localized states.

5. Conclusion

ESR and conductivity experiments, performed on the same $\text{Li}_x\text{V}_2\text{O}_5$ single crystal, suggest the presence of two kinds of charge carriers:

- (i) bound polarons trapped on four vanadium sites around the Li^+ impurity,
- (ii) free polarons hopping between vanadium sites that are not associated with the Li^+ ions.

They show that at low temperature the unpaired electron remains localized in the field of the lithium ion. ESR spectra show that the wave function of this electron is equally delocalized over four vanadium sites. The conductivity is quite low ($\sigma \approx 10^{-10} \Omega^{-1} \text{cm}^{-1}$) and mainly arises from direct hopping of bound polarons between localized states. As the temperature is raised, the thermal energy kT becomes large enough to extract the unpaired electron from the electrostatic field of the lithium. This leads to a lifetime broadening of the ESR spectrum determined by the frequency ν . The corresponding activation energy E determined by linewidth analysis of the ESR spectra leads to $E \approx 0.075$ eV. In the conductivity plot this leads to an increase of the activation energy which has been estimated to $E \approx 0.08$ eV. At high temperature, all small polarons have been freed and move along the vanadium sites with an activation energy $W = 0.21$ eV. This should correspond in the ESR spectra to the continuous broadening arising from spin-lattice relaxation processes described by the frequency Ω .

These results agree quite well with the previous model suggested for non-stoichiometric V_2O_5 [8]. A comparison of both results shows that the activation energy corresponding to the hopping process of free polarons along the vanadium sites does not depend on the nature of the paramagnetic defect. It is about 0.2 eV. The activation energy corresponding to the hopping of bound polarons, on the other hand, appears to depend on the defect. It is somewhat smaller for $\text{Li}_x\text{V}_2\text{O}_5$ ($E = 0.07$ eV) than for non-stoichiometric V_2O_5 ($E = 0.12$ eV). This points out the strong influence of the doping impurity on the localization of the small polaron. It appears that the energy needed to extract the bound polaron from the Coulomb field of the defect decreases when the overall radius of the defect increases.

References

- [1] B. KARVALY and I. HEVESI, *Z. Naturf.* **26a**, 245 (1971).
- [2] P. HAGENMULLER, *Progr. Solid State Chem.* **5**, 71 (1971).
- [3] J. L. RAGLE, *J. chem. Phys.* **38**, 2020 (1963).
- [4] M. VANHAELST and P. CLAUWS, *phys. stat. sol. (b)* **87**, 719 (1978).
- [5] I. B. PATRINA and V. A. IOFFE, *Soviet Phys. — Solid State* **6**, 2581 (1965).
- [6] A. B. SCOTT, J. C. McCULLOCH, and K. M. MAR, *Conductivity in Low Mobility Materials*, Taylor and Francis, London 1971 (p. 107).
- [7] J. HAEMERS, E. BAETENS, and J. VENNIK, *phys. stat. sol. (a)* **20**, 381 (1973).
- [8] C. SANCHEZ, M. HENRY, J. C. GRENET, and J. LIVAGE, *J. Phys. C* **15**, 7133 (1982).
- [9] V. A. IOFFE and I. B. PATRINA, *Soviet Phys. — Solid State* **10**, 639 (1968).
- [10] H. G. BACHMAN, F. R. AHMED, and W. H. BARNES, *Z. Krist.* **115**, 5110 (1961).
- [11] G. SPERLICH and W. D. LAZÉ, *phys. stat. sol. (b)* **65**, 625 (1974).
- [12] V. S. GRUNIN, I. B. PATRINA, and Z. N. ZONN, *phys. stat. sol. (b)* **115**, 545 (1983).
- [13] V. A. IOFFE and I. B. PATRINA, *phys. stat. sol.* **40**, 389 (1970).
- [14] P. NAGELS and M. DENAYER, *Proc. 10th Internat. Conf. Physics of Semiconduction*, Cambridge (Mass.) 1970 (p. 321).
- [15] P. W. ANDERSON, *J. Phys. Soc. Japan* **9**, 316 (1954).
- [16] P. H. ZIMMERMANN, *Phys. Rev. B* **8**, 3917 (1973).
- [17] G. SPERLICH and P. H. ZIMMERMANN, *Solid State Commun.* **14**, 897 (1974).
- [18] D. K. CHAKRABARTY, DIPAK GUTTA, and A. B. BISWAS, *J. Mater. Sci.* **11**, 1347 (1976).
- [19] D. S. VOLZHENSKII and M. V. PASHKOVSKII, *Soviet Phys. — Solid State* **11**, 950 (1969).
- [20] G. SPERLICH, *Z. Phys.* **250**, 335 (1972).
- [21] I. G. AUSTIN and N. F. MOTT, *Adv. Phys.* **18**, 41 (1969).
- [22] J. H. PERLSTEIN, *J. Solid State Chem.* **3**, 217 (1971).
- [23] J. SCHNAKENBERG, *phys. stat. sol.* **28**, 623 (1968).
- [24] J. M. FARLEY and G. A. SAUNDERS, *phys. stat. sol. (a)* **28**, 199 (1975).
- [25] C. SANCHEZ, F. BABONNEAU, R. MORINEAU, J. LIVAGE, and J. BULLOT, *Phil. Mag. B* **47**, 279 (1983).
- [26] J. BULLOT, P. CORDIER, O. GALLAIS, M. GAUTHIER, and J. LIVAGE, *phys. stat. sol. (a)* **68**, 357 (1981).

(Received September 23, 1983)