Zeitschrift:	Helvetica Physica Acta
Band:	58 (1985)
Heft:	2-3
Artikel:	Electronic properties of the III-VI layer compounds and of the transition metal chalcogeno-phosphates MPX
Autor:	Grasso, V. / Girlanda, R.
DOI:	https://doi.org/10.5169/seals-115593

## Nutzungsbedingungen

Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften auf E-Periodica. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. Das Veröffentlichen von Bildern in Print- und Online-Publikationen sowie auf Social Media-Kanälen oder Webseiten ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. <u>Mehr erfahren</u>

## **Conditions d'utilisation**

L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. La reproduction d'images dans des publications imprimées ou en ligne ainsi que sur des canaux de médias sociaux ou des sites web n'est autorisée qu'avec l'accord préalable des détenteurs des droits. <u>En savoir plus</u>

## Terms of use

The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. Publishing images in print and online publications, as well as on social media channels or websites, is only permitted with the prior consent of the rights holders. <u>Find out more</u>

# Download PDF: 31.07.2025

ETH-Bibliothek Zürich, E-Periodica, https://www.e-periodica.ch

# Electronic properties of the III–VI layer compounds and of the transition metal chalcogeno-phosphates MPX<sub>3</sub>

By V. Grasso and R. Girlanda, Instituto di Struttura della Materia dell'Università, Messina, Italy

(17. X. 1984)

In honor of Emanuel Mooser's 60th birthday

Abstract. We briefly discuss some experimental and theoretical aspects of the electronic properties of the III–VI layer compounds GaS, GaSe, InSe and GaTe, as well as of the transition metal chalcogeno-phosphates  $FePS_3$  and  $NiPS_3$ .

A comparative analysis is particularly given of the X-ray photoemisssion spectra of the III–VI layer compounds and of the soft X-ray absorption of  $FePS_3$  and  $NiPS_3$ .

# 1. Introduction

A deeper understanding of the electronic properties of materials of the same family might be provided through a combined analysis of the results of both optical and photoemission experiments and the comparison of band structure calculations performed with the same method and by using the same approximations for all compounds. In this paper, following the above suggestions, we briefly compare some experimental and theoretical aspects of the electronic properties of the III–VI layer compounds, which have been the object of pioneering studies by Prof. E. Mooser. Moreover, we give a comparative analysis of the electronic properties of the transition metal chalcogeno-phosphates FePS<sub>3</sub> and NiPS<sub>3</sub> that are other layer compounds, more recently studied by us.

The III-VI layer compounds GaS, GaSe and InSe crystallize in structures having the same atomic arrangement inside each layer. The different stackings of the layers give the three-dimensional polytypes of different symmetries.

A wealth of experimental information is presently available on the electronic properties of GaS, GaSe and InSe [1]. Photoemission spectroscopy – both integrated [2–5] and angle-resolved [6–10] – proved effective mainly in determining the electronic properties due to the valence states only, and largely – even if not completely – independent of the conduction bands. This suits well with the present status of the band structure calculations, which give quite reliable valence bands, but questionable conduction bands [11–17]. Therefore, the ground-state electronic properties of GaS, GaSe and InSe are quite well understood and only minor details are debated. Conversely, controversial points still exist in the interpretation of some experimental features of the optical spectra, where conduction bands are primarily involved. Thus more detailed information and more refined investigation tools are required to get a better insight into the optical properties of GaS, GaSe and InSe.

Gallium Telluride crystallizes in a monoclinic structure made up by a series of layers bound between themselves by weak van der Waals forces. Within each layer the unit cell contains six formula units, while only two formula units appear in the layer unit cell of the other III–VI layer compounds with hexagonal lattice (GaS, GaSe, and InSe). In spite of this structural difference, many of the electronic properties of GaTe are expected to be analogous to those of GaS, GaSe and InSe. This is mainly due to the fact that in both structures the geometrical arrangement of the nearest neighbour metal and chalcogen atoms is quite similar. The similarity in the electronic properties is enhanced whenever interband matrix elements do not critically affect the response, as in the case of X-Ray Photoemission Spectra (XPS).

# 2. Band structure calculations and XPS measurements of III-VI layer compounds

At the present stage we can say that the band structure of the pure compounds GaS, GaSe – as well as of InSe – are quite satisfactorily established, at least in what the valence bands are concerned, and give a sound basis for discussing also the mixed compounds [18]. GaSe is the most widely studied, and its band structure has been computed both by pseudo-potential procedures [12, 13, 17] and by method of the tight binding type [11, 14–16, 19]. The published bands of GaS have always been obtained in connection with similar computation for GaSe [11, 19], or the whole family GaS, GaSe and InSe [15–17].

In the following we will refer chiefly to a systematic computation of the band of the  $\beta$ -polytypes of the pure compounds [14] made by the overlap reduced semiempirical tight binding (ORSTB) procedure [14, 20]. By this method bands in excellent agreement with the angular resolved photoemission spectra [6–8] were obtained for GaSe and InSe. The bands of GaS were obtained accordingly.

The main features of the method consist in i) neglecting all the three-centre integrals, ii) neglecting the crystal field or, if retained, strongly reducing with respect to the computed one, iii) strongly reducing in magnitude only overlap integrals and retaining the interaction integrals as they are computed. It has been possible to prove that an equivalence exists between the ORSTB and the chemical pseudopotential method [21, 22]. This procedure achieves three main results. First, the relationship between localization of atomic-like orbitals and the semiempirical tight binding is clearly stated, and a short way is suggested to account for localization effects still using free-atom orbitals. Then, while the standard semiempirical tight binding approximations were unrelated and only of practical origin, ORSTB shows that they, once exactly stated, have a common theoretical origin, and cannot be used separately. Finally, the reason is understood why the semiempirical tight binding was so successful, in spite of its quite rough approximations. Conversely, where the semiempirical tight binding fails (as in reproducing the correct width of some bands), ORSTB gives results in excellent agreement with other more sophisticated methods and with experiments.

In Fig. 1 we report jointly the band structures of GaS, GaSe and InSe in order to compare them in their general trends and discuss in the same framework [18]. The valence bands are quite well resolved in four different groups, with different bonding characters and with different contributions from valence atomic orbitals. Their overall shape, however, is similar in all the compounds of the

family, and we will sketch in the following their general properties which do not depend on the specific material. The two valence bands nearest to the optical gap (group A of Fig. 1) show remarkable polarization effects in photoemission [2], in accordance with the strong contribution to the crystal states from  $p_z$  atomic orbitals of the chalcogen, with minor admixture of s and  $p_z$  valence orbitals of the metal. Due to the anisotropy of the crystal field, the  $p_{x,y}$  atomic orbitals of the chalcogen are more bound than the corresponding  $p_z$  orbitals, and give rise mainly to the next eight valence bands (group B in Fig. 1). The strict  $p_{x,y}$  atomic character of the crystal states is limited at and around the  $\Gamma$  point of the Brillouin zone, where the spreading of the B bands is minimum and it is mainly due to the atomic spin-orbit splitting. Near the boundary of the Brillouin zone the spreading of these bands is larger, and the hybridization with other atomic orbitals is relevant.

At higher binding energies two couple of bands occur, both of them being largely formed by s orbitals of the metal. The antibonding bands (group C in Fig. 1) show a large dispersion over the Brillouin zone, and around the point  $\Gamma$  they coincide in energy with some levels of the B bands at the boundaries of the Brillouin zone [6]. On the contrary, the bonding bands (group E, Fig. 1) are quite flat over the whole Brillouin zone.

As to the conduction bands, they are not as well experimentally tested as the valence ones. In addition to the density of states measured by CIS photoemission spectroscopy [2], further experimental information in a range about 8 eV large



## Figure 1

Comparison of the energy band structures of GaS, GaSe and InSe. The energy scale is the same for the three compounds. The dimensions of the Brillouin zones are the appropriate ones for the lattice parameters of each crystal. Broken lines denote bands reproduced from ref. 17. (after (18)).

has been obtained by Piacentini et al. [23] by studying the excitation of the core levels Ga3d and In4d with synchrotron radiation. The experimental results support qualitatively a band scheme for GaS, GaSe and InSe similar to that of Fig. 1, but for the evidence of bands (the couple labelled as B' in Fig. 1) which are not obtained by the Tight Binding (TB) schemes if the basis does not include also functions formed with atomic excited orbitals S4s and Se5s. By adding these orbitals to the TB procedure [15], or by using a pseudopotential approach [12, 13, 17], the bands B' are obtained like those tentatively reproduced in Fig. 1 [17]. They are placed between the first couple of conduction bands (group A' of Fig. 1), which have relevant contributions from s and  $p_z$  orbitals of both metal and chalcogen atoms, and the next group of conduction bands (labelled as C' in Fig. 1), where the largest contribution arises from the metal  $p_{x,y}$  orbitals.

At our knowledge, only two band structures of GaTe have been reported in literature [16, 24].

The main inter-atomic bonds within each layer of GaTe crystals are arranged to give the fundamental structural unit shown in Fig. 2, where each gallium atom is surrounded by another gallium and by three tellurium atoms. Each tellurium atom, in turn, is linked to three nearby gallium atoms, and, in addition, supplies the weaker inter-layer bond with other tellurium centres facing it from the adjacent layer. With minor deformations, this fundamental structure is shared both by the real monoclinic GaTe and by a hexagonal GaSe-like model lattice, even if the overall structure is considerably different in the two cases.

The opportunity of describing GaTe by a simplified hexagonal model has been exploited by Antonangeli et al. [24]. To account for the inter-layer interaction in the model, they assume  $\beta$ -polytype layer packing, which correctly gives for each tellurium centre three nearby tellurium atoms in the adjacent layer, as in the actual monoclinic crystal.

The electronic energy levels, computed by the ORSTB method [24] are reported in Fig. 3 and the valence bands DOS computed by the Lehmann and Taut procedure [25] after the bands of Fig. 3, is reported in Fig. 4.

In Fig. 4, the separate contributions to the DOS of different groups of valence bands are reported. The origin of the main features of the DOS of GaTe is almost the same as in the case of the DOS of the other III-VI layer compounds





Fundamental bonds in GaTe. Solid black circles are gallium atoms, the shaded circles are tellurium atoms.



Figure 3

Band structure of the hexagonal model of GaTe in the  $\beta$  lattice (after ref. (24)). The atomic energies are also indicated.



## Figure 4

Density of states of the valence bands of the hexagonal model of GaTe in the  $\beta$ -polytype, convoluted with a Gaussian distribution with half-width 0.15 eV (upper curve). The lower curves are the separate contributions to the density of states of the single groups of valence bands. Energies are referred to the top of the valence band (after ref. (24)).

with hexagonal lattice [3]. In order to account for the main differences, we first of all note that the atomic eigenvalues of tellurium are less bound than the corresponding ones of sulphur or selenium. At the point  $\Gamma$ , the gap between the groups of A and B bands (refer for labels to Fig. 1) is clearly related to the value of the valence p eigenvalue of the chalcogen; which decreases in magnitude from sulphur to selenium and then to tellurium, while correspondingly the A and B bands become less separated and nearly overlap in GaTe. The 5s atomic level of tellurium (-19.40 eV) is fairly less bound then the 3s one of sulphur (-21.05 eV) and than the 4s one of selenium (-21.42 eV). The position of the peak f in Fig. 4 (12.5 eV in GaS, 13.9 eV in GaSe and 12.0 eV in GaTe) follows the same trend of the atomic levels, in accordance also with the relative experimental positions of the corresponding peak in the three compounds [3, 24]. The other band structure calculation of a model hexagonal GaTe [16] agrees in its gross features with the bands of Fig. 3.

No calculation exists as yet for the monoclinic real structure of gallium telluride.

For comparison in Fig. 5 we report the X-ray photoelectron spectrum of the valence bands and of the Ga3d level of GaTe, as measured by Antonangeli et al. [24]. As previously stated the main features of the photoemission spectrum of the





X-ray photoelectron spectra of the valence bands and the upper metal d-states of a) GaS, b) GaSe, c) InSe and d) GaTe. (after references (3) and (24)).

monoclinic GaTe can be understood by using the hexagonal lattice model, fitted to the extrapolation of the experimental optical data of the mixed  $GaSe_xTe_{1-x}$  compounds. More details could be described by a theoretical DOS computed on the band structure of the monoclinic lattice. In the same figure we report also the analogous measurements for the other III–VI compounds GaS, GaSe and InSe [3].

The origin of the main features of the X-ray photoelectron spectra of GaTe is almost the same as in the case of the other III–VI compounds, with minor differences related principally to the position of the atomic levels, more than to the different atomic structure. For instance, the position of the peak F (14.1 eV in GaS, 13.9 eV in GaSe and 11.5 eV in GaTe) follows the same trend of the atomic s levels of the chalcogen atoms, in accordance also with the relative position of peak f in the theoretical DOS's.

## 3. Transition metal chalcogeno-phosphates MPX<sub>3</sub>

The transition metal chalcogeno-phosphates MPX<sub>3</sub> (M stands for a transition metal ion and X is either sulphur or selenium) form a large family of layered compounds with very interesting properties. In particular, these materials can be intercalated with alkali ions and so they are good candidates in Li-based batteries [26–28]. However, their intercalation capability changes with the transition metal ion. For example, in the case of chemical intercalation, NiPS<sub>3</sub> is the most active material, while ZnPS<sub>3</sub> is completely inert [29]. The S-based compounds crystallize in the monoclinic system and have similar lattice parameters [30, 31]. Their different behaviour with respect to intercalation has been related to the degree of ionicity of the transition metal ion [26]. We feel that it depends strongly also on the number of available d states.

The electronic band structure of the transition metal chalcogeno-phosphates has not been calculated yet. Piacentini et al. [32] proposed a semiempirical molecular orbital scheme for the  $(P_2S_6)^{4-}$  cluster in NiPS<sub>3</sub>. Group theory was used to derive the symmetrized combinations of the phosphorous 3s, 3p and the sulphur 3s, 3p states. After identifying the bonding and antibonding combinations, an energy level sequence of the valence states was proposed. Finally, the energies of the levels were obtained empirically from the comparison with the valence band X-ray photoemission spectra. This approach gave a reliable sequence of the valence states, but it could not give an accurate description of the localized transition metal 3d states and of the lowest conduction states, based primarily on the transition metal 4s and 4p levels and on the phosphorous and sulphur 3p, levels [33]. Hints on the conduction bands density of states were obtained by a comparative analysis of the reflectivities of several MPS<sub>3</sub> compounds measured up to 35 eV [34]. Piacentini et al. [35] measured the soft X-ray absorption spectra of pure FePS<sub>3</sub> and NiPS<sub>3</sub> at the PL<sub>2.3</sub>, SL<sub>2.3</sub>, SL<sub>1</sub>, and  $Fe(Ni)M_{2,3}$  thresholds.

The phosphorous and sulphur  $L_{2,3}$  absorption spectra are very alike in the two compounds and between each other, indicating that they do not depend on the transition metal ion, but that they represent the density of the first empty states of the  $(P_2S_6)^{4-}$  cluster. From the relative intensities of the structures, one can think that the lowest conduction band is formed mostly by phosphorous *s*-like



Figure 6

Absorption spectra of the  $PL_{2,3}$ ,  $SL_{2,3}$  and  $SL_1$  core states of FePS<sub>3</sub> (left panels) and NiPS<sub>3</sub> (right panels). The  $PL_{2,3}$  spectrum of NiPS<sub>3</sub> shows also the direct photoemission peak. The dashed curve under this peak represents the most probable absorption spectrum, as inferred by a comparison with the yield spectrum taken at 0.8 eV kinetic energy. (after ref. (35)).

states. Instead, the transition metal  $M_{2,3}$  edges are atomic-like and strongly affected by final state configuration interaction.

In Fig. 6 we present the normalized absorption spectra of the P  $L_{2,3}$ , S  $L_{2,3}$ , and S  $L_1$  core states in FePS<sub>3</sub> and NiPS<sub>3</sub>, after Piacentini et al. [35].

It is remarkable that the spectra of the core states of FePS<sub>3</sub> shown in Fig. 6 are practically the same as those of NiPS<sub>3</sub>. In addition, the main features of the P L<sub>2,3</sub>, S L<sub>2,3</sub> and S L<sub>1</sub> spectra in both compounds occur at almost the same renormalized energies, but with different relative intensities. Both observations are strong indications that these spectra are affected only slightly by the transition metal ion and that they represent the projected densities of states of the (P<sub>2</sub>S<sub>6</sub>)<sup>4-</sup> clusters [35].

The M<sub>2,3</sub> spectra of Fe and Ni in FePS<sub>3</sub> and NiPS<sub>3</sub>, shown in Fig. 7, differ significantly from each other and from the P and S L<sub>2,3</sub> edges. Instead, resemble very much the M<sub>2,3</sub> absorptions of Fe and Ni in several other ionic compounds, such as their halides and oxides [36, 37], suggesting that the transition metal ion M<sup>++</sup> spectra represent an intra-atomic character of the excitation, irrespective of the ligand species. Thus, the sharp fine structures are interpreted in terms of the transition metal ion intra-atomic transitions  $3p^63d^m-3p^53d^{m+1}$  (m = 6 for Fe<sup>++</sup>, and m = 8 for Ni<sup>++</sup>), that is split into a multiplet structure by multiconfigurational interaction of the final state  $3p^53d^{m+1}$ .

For a detailed discussion of the electronic properties of these compounds we refer to the work by Piacentini et al. [35, 38] and references quoted therein.



Figure 7

Absorption spectra of the Fe (upper curve) and Ni (lower curve)  $M_{2,3}$  core states in FePS<sub>3</sub> and NiPS<sub>3</sub>, respectively. The dashed curves reproduce the spectra calculated by Yamaguchi et al. (39) for the respective halides. The inset in the NiPS<sub>3</sub> panel is the second-order P L<sub>2,3</sub> spectrum as measured in the Fe M<sub>2,3</sub> spectrum in FePS<sub>3</sub>. (after ref. (35)).

#### REFERENCES

- 1. Refer, for instance, to the volumes of the series Physics and Chemistry of Materials with Layered Structures, E. Mooser, general editor (Boston, Mass.). In particular, for reviews of the experimental and of the theoretical progress on the electronic properties, see, respectively, Optical and Electric Properties, edited by P. A. Lee, 4 (Boston, Mass. 1976) and Electrons and Phonons in Layered Crystal Structures, edited by T. J. Wieting and M. Schlüter, 3 (Boston, Mass., 1979). The most recent developments reviewed in Electronic Structure and Electronic Transitions in Layered Materials: Recent Developments, edited by V. Grasso, to appear.
- 2. G. MARGARITONDO, J. E. ROWE and S. B. CHRISTMAN, Phys. Rev. B, 15, 3844 (1977).
- 3. F. ANTONANGELI, M. PIACENTINI, A. BALZAROTTI, V. GRASSO, R. GIRLANDA and E. DONI, Nuovo Cimento B, 51, 181 (1979). Further references are quoted therein.
- 4. G. MARGARITONDO, F. LEVY, N. G. STOFFEL and A. KATNANI, Phys. Rev. B, 21, 5768 (1980).
- 5. G. MARGARITONDO, A. D. KATNANI, N. G. STOFFEL, F. LEVY and I. ABBATI, Solid State Commun. 33, 641 (1980).
- 6. P. K. LARSEN, G. MARGARITONDO, J. E. ROWE, M. SCHLÜTER and N. V. SMITH, Phys. Lett. A, 58, 423 (1976).
- 7. P. THIRY, Y. PETROFF, R. PINCHAUX, C. GUILLOT, Y. BALLU, J. LACANTE, J. PAIGNÉ and F. LEVY, Solid State Commun. 22, 685 (1977).
- 8. P. K. LARSEN, S. CHIANG and N. V. SMITH, Phys. Rev. B, 15, 3200 (1977).
- 9. J. F. MCGILP and A. W. PARKE, Phys. Status Solidi B, 94, 685 (1979).
- 10. J. E. ROWE and G. MARGARITONDO, unpublished data on GaS.
- 11. F. BASSANI and G. PASTORI PARRAVICINI, Nuovo Cimento B, 50, 95 (1967).
- 12. M. SCHLÜTER, Nuovo Cimento B, 13, 313 (1973).

- 13. M. SCHLÜTER, J. CAMASSEL, S. KOHN, J. P. VOITCHOVSKY, J. R. SHEN and M. L. COHEN, Phys. Rev. B, 13, 3534 (1976).
- 14. E. DONI, R. GIRLANDA, V. GRASSO, A. BALZAROTTI and M. PIACENTINI, Nuovo Cimento B, 51, 154 (1979). Other band structure calculations published up to 1978 are quoted therein.
- 15. S. NAGEL, A. BALDERESCHI and K. MASCHKE, J. Phys. C, 12, 1626 (1979).
- 16. J. ROBERTSON, J. Phys. C, 12, 4777 (1979).
- 17. Y. DEPEURSINGE, Nuovo Cimento B, 64, 111 (1981). See also Y. DEPEURSINGE, Thèse, Ecole Polytechnique Fédérale, Lausanne, 1978.
- 18. A. M. MANCINI, A. RIZZO, R. GIRLANDA, G. GUIZZETTI, L. NOSENZO, E. DONI and E. REGUZZONI, Nuovo Cimento D, 1, 751 (1982).
- 19. H. KAMINURA and N. NAKAO, J. Phys. Soc. Jpn. 21 Suppl. 27 (1966).
- 20. E. DONI, R. GIRLANDA and L. RESCA, J. Phys. Soc. Jpn. 49 (Suppl. A) 89 (1980).
- 21. P. W. ANDERSON, Phys. Rev. 181, 25 (1969).
- 22. J. D. WEEKS, P. W. ANDERSON and A. G. H. DAVIDSON, J. Chem. Phys. 58, 1388 (1973).
- 23. M. PIACENTINI, C. G. OLSON, A. BALZAROTTI, R. GIRLANDA, V. GRASSO and E. DONI, NUOVO Cimento B 54, 248 (1979).
- 24. F. ANTONANGELI, A. BALZAROTTI, E. DONI, R. GIRLANDA, V. GRASSO and M. PIACENTINI, Physica B & C 105, 59 (1981).
- 25. G. LEHMANN and M. TAUT, Phys. Stat. Sol. B 54, 469 (1972).
- 26. R. BREC, G. OUVARD, A. LOUISY, J. ROUXEL, and A. LE MEHAUTE, Solid State Ionics 6, 185 (1982).
- 27. G. OUVRARD, Thesis, Nantes (1980), unpublished.
- 28. A. LOUISY, Thesis, Nantes (1981), unpublished.
- 29. R. BREC, D. M. SCHLEICH, G. OUVRARD, A. LOUISY and J. ROUXEL, Inorg. Chem. 18, 1814 (1979).
- 30. W. KLINGEN, G. EULENBERGER and H. HAHN, Naturwissenschaften 55, 229 (1968).
- 31. W. KLINGEN, G. EULENGERGEN and H. HAHN, Naturwissenschaften 57, 88 (1970).
- 32. M. PIACENTINI, F. S. KHUMALO, C. G. OLSON, J. W. ANDEREGG and D. W. LYNCH, Chem. Phys. 65, 289 (1982).
- 33. F. S. KHUMALO and H. P. HUGHES, Phys. Rev. B 23, 5375 (1981).
- 34. M. PIACENTINI, F. S. KHUMALO, G. LEVEQUE, C. G. OLSON and D. W. LYNCH, Chem. Phys. 72, 61 (1982).
- M. PIACENTINI, V. GRASSO, S. SANTANGELO, M. FANFONI, S. MODESTI and A. SAVOIA, Solid State Commun. 51, 467 (1984).
- 36. S. SHIN, S. SUGA, H. KANZAKI, S. SHIBUYA and T. YAMAGUCHI, Solid State Commun. 38, 1281 (1981).
- 37. S. SHIN, S. SUGA, M. TANIGUCHI, H. KANZAKI, S. SHIBUYA and T. YAMAGUCHI, J. Phys. Soc. Jpn. 51, 906 (1982).
- 38. M. PIACENTINI, V. GRASSO, S. SANTANGELO, M. FANFONI, S. MODESTI and A. SAVOIA, Nuovo Cimento D, to be published.
- 39. T. YAMAGUCHI, S. SHIBUYA, S. SUGA and S. SHIN, J. Phys. C 15, 2641 (1982).