

Tunnelling spectroscopy investigation of the CDW state in $\text{TiSe}_{2-x}\text{S}_x$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1996 J. Phys.: Condens. Matter 8 7453

(<http://iopscience.iop.org/0953-8984/8/40/010>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.207

The article was downloaded on 14/05/2010 at 04:15

Please note that [terms and conditions apply](#).

Tunnelling spectroscopy investigation of the CDW state in $\text{TiSe}_{2-x}\text{S}_x$

Y Miyahara[†], H Bando and H Ozaki

Department of Electrical, Electronics and Computer Engineering, Waseda University, Ohkubo 3-4-1, Shinjuku-ku, Tokyo 169, Japan

Received 10 June 1996, in final form 29 July 1996

Abstract. Tunnelling spectroscopy measurements were carried out on the mixed crystal $\text{TiSe}_{2-x}\text{S}_x$ ($0 \leq x \leq 0.55$) to investigate the change in the density of states in the CDW state. The temperature dependences of the CDW energy gap widths were obtained. Experiments showed that the flattening of the peak in the ρ - T curve with increasing x corresponds to the decrease in the CDW energy gap. A model was proposed in which the anomalous ρ - T characteristics in this system were explained in terms of the competition of the two conduction mechanisms associated with the metallic carriers and the 'excitonic' carriers.

1. Introduction

The layered-structure material TiSe_2 is one of the group-IVB transition metal dichalcogenides, and it is well known for its characteristic CDW phase transition which occurs at around 200 K (Di Salvo *et al* 1976). In layered materials, the CDW phase transition in the group-VB transition metal dichalcogenides is well understood within the framework of the nesting mechanism. Group-VB materials have metallic band structures in the normal phase, and it is considered that their two-dimensional Fermi surfaces with strong anisotropy which are suitable for nesting lead to the CDW transition.

On the other hand, considering the atomic valence, group-IVB materials should be semiconductors with p-d gaps. In the case of the titanium group, the band calculation predicts that TiS_2 is a semiconductor with a band gap of about 0.3 eV (Zunger and Freeman 1977), and that TiSe_2 and TiTe_2 are semimetals with band overlaps of about 0.2 eV (Zunger and Freeman 1978) and 0.5 eV (Bullet 1978), respectively. Many studies have been made already on TiSe_2 and TiS_2 , and it is well established that only TiSe_2 undergoes the CDW transition (Di Salvo *et al* 1976, Brown 1980).

The CDW transition in TiSe_2 has characteristic features. One is that TiSe_2 has no incommensurate phase. Although several models have been proposed for the mechanism of this phase transition, a decisive conclusion has not been reached yet. It has been pointed out that TiSe_2 has a positive band overlap, unlike TiS_2 , and that this fact is crucial for the phase transition (Wilson 1978). Many experiments have been tried with the aim of changing the band overlap by preparing mixed crystals of TiSe_2 and other transition metal dichalcogenides with band gaps. For example, $\text{Ti}_{1-x}\text{Hf}_x\text{Se}_2$, a mixed crystal of TiSe_2 and the semiconductor HfSe_2 , was prepared and some studies have been made to investigate the change of the CDW phase transition with x (Taguchi 1979, 1981, Borghesi *et al* 1984,

[†] E-mail address: miyahara@ozaki.elec.waseda.ac.jp.

Taguchi *et al* 1984, Starnberg *et al* 1987, Law *et al* 1991). Similar studies have also been made on $\text{TiSe}_{2-x}\text{S}_x$. It is known that $\text{TiSe}_{2-x}\text{S}_x$, a mixed crystal of TiSe_2 and the semiconductor TiS_2 , can be prepared in the composition range $0 \leq x \leq 2$, and its lattice constants change linearly with x (Rimmington and Balchin 1974). Based on the assumption that the band overlap (gap) changes linearly with x , the band overlap is expected to vanish at around $x = 0.8$. A former study on this system by Di Salvo *et al* (1976) reported that the phase transition disappeared at $x = 0.95$.

However, in many such studies, the changes of the phase transition have been discussed only on the basis of transport properties, and only a few experiments have been carried out using spectroscopic techniques such as optical absorption (Taguchi *et al* 1984, Borghesi *et al* 1984) in order to investigate the electronic structure directly.

In a previous study, we carried out a tunnelling spectroscopy investigation of pure TiSe_2 ($x = 0$) and demonstrated the temperature dependence of the CDW energy gap (Miyahara *et al* 1995). In the present study, $\text{TiSe}_{2-x}\text{S}_x$ crystals were prepared, and their electronic structures were investigated using tunnelling spectroscopy. We report the x -dependence of the CDW energy gap, and discuss its correlation with the resistivity-temperature characteristics.

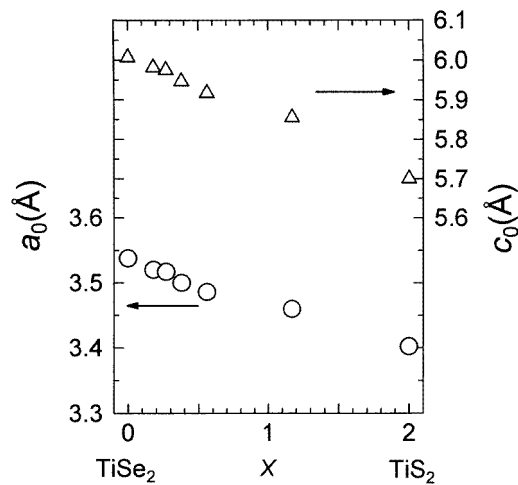


Figure 1. The lattice parameters a_0 and c_0 for the mixed system $\text{TiSe}_{2-x}\text{S}_x$ as a function of S composition x .

2. Experiments

2.1. Crystal growth

$\text{TiSe}_{2-x}\text{S}_x$ single crystals were prepared by the chemical vapour transport method using iodine as the transport agent. Stoichiometric amounts of the powder elements (purities: Ti: 99.99%; Se: 99.999%; S: 99.999%) were sealed into a quartz ampoule under vacuum (6×10^{-6} Torr), and then heated to 710 °C for 120 hours. The resulting polycrystal powder was sealed into a quartz ampoule with amounts of excess Se and S of 5 mg per cm^3 of ampoule volume. Then the ampoule was heated to 650 °C for about 240 hours. The crystal obtained was typically about $4 \times 4 \text{ mm}^2$ in size, and 0.5–1.0 mm in thickness, and its

hexagonal shape reflected the crystal structure. For S content $x \leq 1$, some single crystals were obtained after the first step. These crystals, which did not contain iodine, were also employed for the measurements.

The chemical compositions of the crystals obtained were analysed by electron probe microanalysis, and the lattice constants were obtained by powder x-ray diffraction analysis.

2.2. ρ - T measurement

In order to confirm the CDW transition and estimate the transition temperature, we measured the temperature dependences of the electrical resistivity perpendicular to the c_0 -axis in the temperature range 10–350 K by use of the Van der Pauw technique. The first derivatives of the resistivity–temperature curves were also obtained by numerical differentiation.

2.3. Tunnelling measurement

Tunnelling spectroscopy measurements were carried out in the same manner as in our previous study. We employed the planar contact technique with a counter-electrode of Al/Al oxide. The detail of this technique was given in our previous paper (Miyahara *et al* 1995). All of the measurements were carried out in the temperature range 77–295 K in a helium gas atmosphere. The standard modulation technique was used to obtain the differential conductance dI/dV - V characteristics.

3. Experimental results

3.1. Lattice constants

In order to estimate the lattice constants of the samples prepared, powder x-ray diffraction measurements were carried out. The x -dependences of the lattice constants are shown in figure 1. Hereafter we employ the value of x determined from electron probe microanalysis measurements on the single-crystal samples as the S composition. As shown in figure 1, the lattice constants of both the a_0 - and c_0 -axes change almost linearly with x . Furthermore, a break appears to be present at $x \simeq 0.8$ as pointed out by Wilson (1978). It is considered that this break is associated with p-d overlap.

3.2. ρ - T characteristics

Figure 2 shows the electrical resistivity versus temperature characteristics for various values of x . All of the curves are normalized with respect to each resistivity at 300 K. The extrema of these curves are known to indicate the strength of the CDW phase transition. It is considered that this resistivity anomaly is caused by the reduction of the density of states near the Fermi level associated with the formation of the CDW energy gap. As shown in this figure, these extrema decrease rapidly with increasing x . It should be noticed that the ρ - T curves for the samples with $x = 0$ and $x = 0.27$ have characteristics deviating from the behaviours in the series of other samples because these two samples were prepared without iodine.

To estimate the critical temperature from the ρ - T curves, we calculated the first derivatives of these curves. The results are shown in figure 3. The peak temperature goes down to lower temperature with increasing x (the samples with $x = 0$ and $x = 0.27$ contain no iodine). A steep change occurs between $x = 0.38$ and $x = 0.55$, and the peak structures in the ρ - T curve are blurred for $x \geq 0.55$.

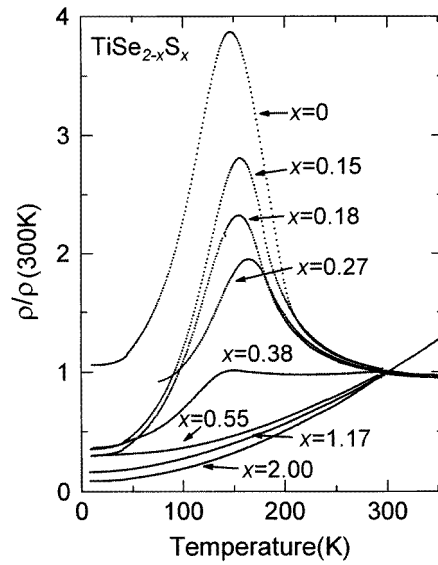


Figure 2. Temperature dependences of the resistivity normalized at 300 K for the single crystals $\text{TiSe}_{2-x}\text{S}_x$.

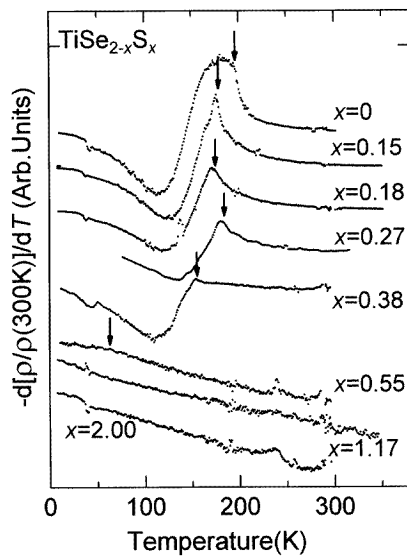


Figure 3. Temperature dependences of $-d\rho/dT$ for $\text{TiSe}_{2-x}\text{S}_x$. The arrows mark the critical temperatures T_c .

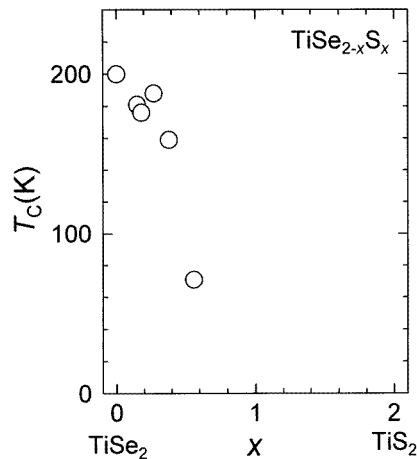


Figure 4. The critical temperature T_c determined from figure 3 as a function of S composition x for the mixed system $\text{TiSe}_{2-x}\text{S}_x$.

According to Di Salvo's result (Di Salvo *et al* 1976), the temperature of the sharp bend in the ρ - T curve corresponds to the critical temperature. Referring to this, we estimated the critical temperature for each sample from the peak temperatures of $-d^2\rho/dT^2$ against T obtained from figure 3. Figure 4 shows the thus-obtained x -dependence of the critical

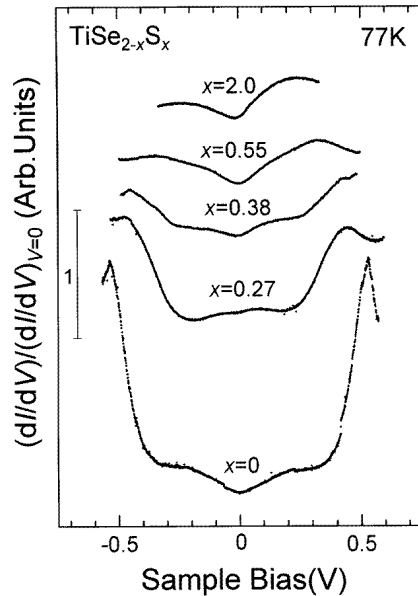


Figure 5. Tunnelling spectra of $\text{TiSe}_{2-x}\text{S}_x$ at 77 K.

temperature T_c . It can be seen that T_c begins to decrease rapidly at around $x = 0.4$. Furthermore, from the extrapolation of the plots in figure 4, the phase transition seems to disappear at around $x = 0.6$.

3.3. Tunnelling characteristics at 77 K

Tunnelling spectroscopy measurements were carried out on the samples with $x = 0.27$, $x = 0.38$, $x = 0.55$ and $x = 2.0$. As shown in figures 2 and 3, the $\rho-T$ characteristics strongly change over the range $0 \leq x \leq 0.55$. Corresponding to this, a strong change in the tunnelling spectrum is expected.

Figure 5 shows the $dI/dV-V$ characteristics obtained at 77 K. All of the spectra are normalized with respect to each dI/dV at $V = 0$, and shifted vertically for clarity. As can be seen in the spectrum of the sample with $x = 0$, the density of states falls sharply in the energy range of ± 0.5 eV around the Fermi level. This indicates the formation of the energy gap associated with the occurrence of the CDW.

It can be noted that, with increasing x , the gap width decreases and the number of states inside the gap increases. The peak structures at the gap edges are sharp at $x = 0$, and broadened with increasing x . Furthermore, while the profiles of the tunnelling spectra for the range $0 \leq x \leq 0.38$ are similar, those for $x \geq 0.55$ are very different. This corresponds to the steep change in the $\rho-T$ characteristics.

3.4. Temperature dependence of tunnelling spectra

The tunnelling spectra for $x = 0.27$, 0.38 and 0.55 for various temperatures are shown in figure 6, (a)–(c). In each panel, the gap width tends to become narrower with increasing temperature. In order to estimate the scale of these behaviours, we defined the gap width

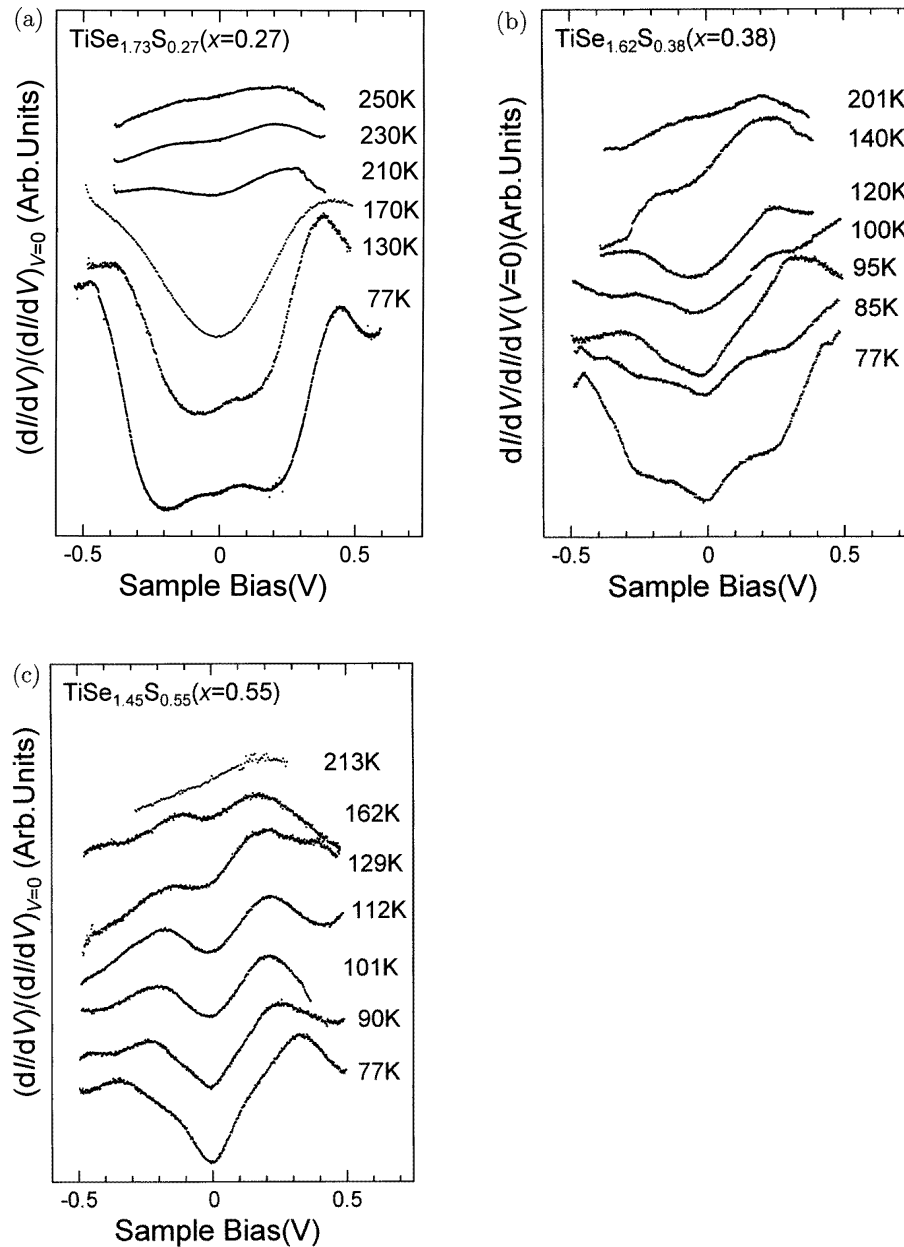


Figure 6. (a) Tunnelling spectra of $\text{TiSe}_{2-x}\text{S}_x$ ($x = 0.27$) at various temperatures. (b) Tunnelling spectra of $\text{TiSe}_{2-x}\text{S}_x$ ($x = 0.38$) at various temperatures. (c) Tunnelling spectra of $\text{TiSe}_{2-x}\text{S}_x$ ($x = 0.55$) at various temperatures.

as the separation of the bias voltages at which the $dI/dV-V$ curve has maximum slope for both bias polarities, and plotted the gap width versus temperature in figure 7. The bars in figure 7 show each of the T_c determined from the $\rho-T$ curves in figure 3. From this, it can be noted that the gap width closely corresponds to T_c .

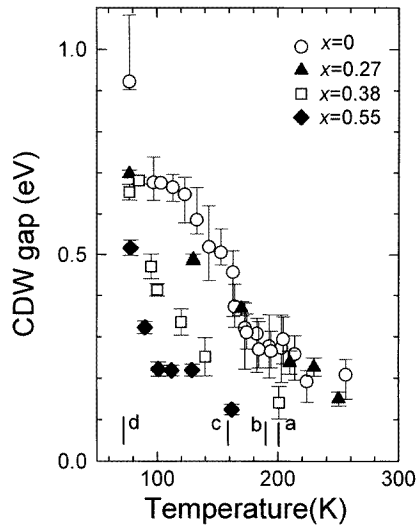


Figure 7. The temperature dependences of the CDW energy gaps for $\text{TiSe}_{2-x}\text{S}_x$ ($x = 0, 0.27, 0.38$ and 0.55). The bars a, b, c and d show T_c for $x = 0, x = 0.27, x = 0.38$ and $x = 0.55$, respectively.

4. Discussion

As shown in figure 5, two gap structures with the gap widths ± 0.5 V and ± 0.1 to ± 0.2 V appear in the spectrum for $x = 0$. The density of states left in the larger gap has a smeared gap structure. This structure was observed above T_c , where the larger gap structure diminished. This smaller gap structure is related to CDW fluctuations as discussed in our previous paper. The smaller gap structure was very sensitive to the condition of the tunnelling junction, and it was, in some cases, hard to observe. Similarly, these two structures appear in the spectra for both $x = 0.27$ and $x = 0.38$. The larger gap structure with the sharp rise of dI/dV becomes obscure in the spectra for $x = 0.55$ and $x = 2.0$. This corresponds to the flattening of the peaks of the $\rho-T$ curves for $x \geq 0.55$.

In our previous study, both the larger and the smaller gap structures were shown for TiSe_2 ($x = 0$). Looking at the result for the sample with $x = 0$ in figure 7, the gap width increases slowly with decreasing temperature from room temperature, and increases rapidly below ≈ 170 K. This behaviour was explained by assuming the existence of two gap structures, of which the smaller had a weak temperature dependence of the gap width, and the larger started to grow sharply below $T_c = 200$ K. We postulated that the larger and the smaller gap structures corresponded to the locked-in CDW gap and the pseudo-gap originating from CDW fluctuations, respectively. Similar results were obtained for the samples with $x = 0.27$ and $x = 0.38$. On the other hand, in the case where $x = 0.55$ with $T_c = 70$ K, the larger gap structure with the sharp rise of dI/dV was not observed in figure 6(c). In this case, the measuring temperature 77 K seemed not to be low enough for us to observe the larger gap structure clearly. However, we cannot expect the larger gap structure to appear far below T_c , because the temperature dependence of $d\rho/dT$ changes drastically at $x = 0.55$ from those for smaller x .

In figure 5, the larger gap width becomes narrower and its depth becomes shallower with increasing x . In other words, finite electronic states remain inside the CDW gap, and they

increase in number with increasing x . It is considered that the carriers in the remaining states inside the gap (we call them the remaining carriers) contribute to the electric conduction and govern the ρ - T characteristics in the low-temperature region. Actually, the resistivity peaks in the ρ - T curves have been attributed to the competition between the decrease in carrier concentration associated with the formation of the CDW gap and the decrease in the scattering rate of the remaining carriers owing to the lowering of the temperature. Thus, we can assume two components of the carriers. One is that which can contribute to the CDW condensation in the low-temperature phase, and the other is the remaining carrier at the Fermi level inside the gap which has a metallic nature with weak CDW fluctuations over the whole temperature range. It is considered that the former component originates from electrons which can interact with holes, according to the excitonic insulator transition mechanism suggested by Wilson (1977). He pointed out the anomalous behaviour of the CDW transition in TiSe_2 , as follows. In contrast with the group-VB materials whose CDW transition mechanisms are governed by a Fermi-surface-driven mechanism, the CDW transition in TiSe_2 does not enter an incommensurate phase, and the periodicity of the CDW is not affected by the adjustment of the Fermi surface through the carrier doping. In such a situation, the excitonic insulator transition mechanism has been argued as being one of the possible mechanisms for the CDW transition in TiSe_2 proposed so far. This is based on the prediction that the direct Coulomb interaction between the electrons and the holes will lead to a certain instability at low temperature (Halperin and Rice 1968). Thus, we call the carriers which contribute to the CDW condensation ‘excitonic’ carriers, hereafter. The x -dependence of the ρ - T characteristics can be explained qualitatively on the basis of this assumption. The ‘excitonic’ carriers exhibit semiconducting ρ - T characteristics after the occurrence of the instability. On the other hand, the remaining carriers, which cannot contribute to the instability, have metallic ρ - T characteristics. In this situation, the ρ - T characteristics with the peaks are governed by the ratio of these two carrier components. If the number of ‘excitonic’ carriers is relatively small, the resistivity peak in the ρ - T curve, which originates from the ‘excitonic’ carriers, will be suppressed since the conduction by the remaining carriers becomes dominant.

The ratio of the two components is affected by the band overlap and/or the additional doping of carriers. In the interpretation of the present results, we assume that we have observed the effect of the change in the band overlap in the normal state rather than that of the additional carrier doping. This assumption is considered to be reasonable because our crystal growth was carried out at a lower temperature (650 °C), so the number of additional carriers doped by the temperature-induced defects was not significant (Di Salvo *et al* 1976).

As the band overlap decreases with increasing x , the number of ‘excitonic’ carriers decreases. This is caused by the imbalance between the numbers of electrons and of holes. Thus, the flattening of the resistivity peak in the ρ - T curve with increasing x can be explained.

5. Conclusion

The tunnelling spectra of $\text{TiSe}_{2-x}\text{S}_x$ in the low-temperature region show that the CDW energy gap structure becomes obscure with increasing x . This tendency indicates that the proportion of the carrier component which can contribute to the CDW condensation decreases with increasing x . Thus, our present study has explained the effect of the change in the band overlap in the normal state on the CDW phase transition in terms of the imbalance between the electrons and the holes which can be ‘excitonic’ carriers.

Acknowledgment

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science and Culture.

References

- Borghesi A, Geddo M, Guizzetti G, Ruguzzoni E, Stella A and Lévy F 1984 *Phys. Rev. B* **29** 3167
Brown F C 1980 *Physica B* **99** 264
Bullet D W 1978 *J. Phys. C: Solid State Phys.* **11** 4501
Di Salvo F J, Moncton D E and Waszczak J V 1976 *Phys. Rev. B* **14** 4321
Halperin B I and Rice T M 1968 *Rev. Mod. Phys.* **40** 755
Law A R, Hughes H P, Andrews P T and Lévy F 1991 *Solid State Commun.* **78** 599
Margaritondo G, Bertoni C M, Weaver J H, Lévy F, Stoffel N G and Katnani A D 1981 *Phys. Rev. B* **23** 3765
Miyahara Y, Bando H and Ozaki H 1995 *J. Phys.: Condens. Matter* **7** 2553
Rimington H P B and Balchin A A 1974 *J. Cryst. Growth* **21** 171
Starnberg H I, Johnson M T, Friend R H, Hughes H P and Lévy F 1987 *J. Phys. C: Solid State Phys.* **20** 1483
Taguchi I 1979 *Solid State Commun.* **32** 679
———1981 *J. Phys. C: Solid State Phys.* **14** 3221
Taguchi I, Vaterlaus H P and Lévy F 1984 *Solid State Commun.* **49** 79
Wilson J A 1977 *Commun. Phys.* **2** 23
———1978 *Phys. Status Solidi b* **86** 11
Zunger A and Freeman A J 1977 *Phys. Rev. B* **16** 906
———1978 *Phys. Rev. B* **17** 1839