Transport properties of icosahedral $Al_{70}Pd_{22.5}Re_{7.5}$ quasicrystals

Transport properties of icosahedral $Al_{70}Pd_{22.5}Re_{7.5}$ quasicrystals

Y K Kuo[1], J R Lai[1], C H Huang[2], C S Lue[2] and S T Lin[2]

[1] Department of Physics, National Dong Hwa University, Hualien 97401, Taiwan
[2] Department of Physics, National Cheng Kung University, Tainan 70101, Taiwan

Abstract
We report the electrical and thermal transport properties, including electric
resistivity (ρ), Seebeck coefficient (S) and thermal conductivity (κ) of
icosahedral $Al_{70}Pd_{22.5}Re_{7.5}$ quasicrystals in the temperature range between
10 and 300 K. Four $Al_{70}Pd_{22.5}Re_{7.5}$ samples with a resistivity ratio $\Re =
\rho_{4.2\ K}/\rho_{300\ K}$ ranging from 10.2 to 84.4 were studied. The temperature-
dependent resistivities increase with decreasing temperature for all samples,
exhibiting a semiconductor-like behaviour. The Seebeck coefficients are
positive for the large-$\Re$ samples ($\Re = 26.3$ and 84.4) in the entire temperature
range, while S-values become negative for the small-$\Re$ samples ($\Re = 10.2$
and 19.4) below about 120 K. The significant dependence on $\Re$ of the Seebeck
coefficient can be qualitatively understood in the pseudogap scenario. The
temperature variation of the thermal conductivity for these materials is quite
similar, with values less than 2.5 W m^{-1} K^{-1} in the temperature range we
investigated. The dimensionless thermoelectric figure of merit (ZT) of this
system is estimated to be two orders of magnitude smaller than that of
conventional thermoelectric materials.

1. Introduction

The electrical and thermal transport properties of quasicrystals have attracted considerable
attention due to the peculiar electronic and thermal properties they exhibit [1]. In general,
quasicrystals exhibit low thermal conductivities (κ) due to their quasicrystalline structures
and scattering on heavy ions, moderate electrical resistivities (ρ), and relatively high absolute
magnitudes of the Seebeck coefficient (S). Since the potential of a material for thermoelectric
applications is determined by the thermoelectric figure of merit $ZT = (S^2/\rho\kappa)T$, the
thermoelectric characteristics of quasicrystals seem to meet the criterion of being a potentially
good thermoelectric material.

It is well known that the electrical conductivity and Seebeck coefficient of quasicrystals
are very sensitive to the chemical composition and heat treatment of the sample. Therefore,

one can adjust these two transport properties of quasicrystals by varying the composition and/or annealing condition without sacrificing their low thermal conductivity. Recent theoretical studies also suggest that high ZT-values may be achieved for quasicrystalline alloys [2, 3]. Such an encouraging result motivates intensive experimental investigations on the thermoelectric properties of various quasicrystals [4–14]. For example, the thermoelectric properties of AlPdMn icosahedral quasicrystal have been studied and the results indicated that this system could be a promising candidate for a thermoelectric material [4].

Icosahedral AlPdRe quasicrystals have the highest low-temperature resistivity ($\rho_{4.2 \text{ K}} = 2 \text{ } \Omega \text{ cm}$) at 4.2 K [15] and resistivity ratio $\Re = \rho_{4.2 \text{ K}}/\rho_{300 \text{ K}}$ ($\sim$280) [16] among the known quasicrystals. Studies of the composition dependence of the thermoelectric properties in AlPdRe quasicrystals at high temperatures (300 K $< T <$ 900 K) have been performed previously [12, 13]. It was found that the thermoelectric figure of merit of AlPdRe quasicrystals has a maximum value of approximately 0.1, about one-tenth that of the best-known thermoelectric materials such as Bi_2Te_3. The ZT-value shows strong composition dependence, varying by about two orders of magnitude with a slight change in Re concentration or additional ruthenium in the AlPdRe icosahedral phase [12]. It was proposed that a possible improvement of thermoelectric performance could be made through fine-tuning the composition of these quasicrystals [12]. In this paper, we present the measurements of electrical and thermal transport properties, including electric resistivity, Seebeck coefficient, and thermal conductivity, in the temperature range between 10 and 300 K of icosahedral $Al_{70}Pd_{22.5}Re_{7.5}$ quasicrystals with different annealing conditions. Four different annealing $Al_{70}Pd_{22.5}Re_{7.5}$ samples with resistivity ratio $\Re = 10.2, 19.4, 26.3$ and 84.4 were studied. It is found that the temperature-dependent resistivity and Seebeck coefficient show strong $\Re$ dependence, while the thermal conductivity is essentially unaffected for samples with different $\Re$. The room-temperature thermoelectric figure of merit is larger with increasing $\Re$ due to the higher value of the Seebeck coefficient for the large-$\Re$ sample, but is still small compared to that of conventional thermoelectric materials.

2. Experiment

Ingots of $Al_{70}Pd_{22.5}Re_{7.5}$ alloys were obtained by arc melting of a mixture of high purity elements in a purified argon atmosphere. Icosahedral $Al_{70}Pd_{22.5}Re_{7.5}$ quasicrystals were then prepared by annealing these ingots in vacuum at 980 °C for 24 h. For preparing good-quality samples with $\Re > 40$, a further annealing at around 600 °C for several hours was required. An x-ray analysis taken with Cu Kα radiation showed that all prepared samples were single-phased and consistent with the expected icosahedral structure. Detailed descriptions of the sample preparation and x-ray diffraction patterns of $Al_{70}Pd_{22.5}Re_{75}$ quasicrystals can be found elsewhere [17].

Resistivity data were obtained by a standard dc four-terminal method. Seebeck coefficient measurements were performed with a dc pulse technique. Seebeck voltages were detected using a pair of thin Cu wires electrically connected to the sample with silver paint at the same positions as the junctions of the differential thermocouple. The stray thermal emfs are eliminated by applying long current pulses ($\sim$100 s) to a chip resistor that serves a heater, where the pulses appear in an off–on–off sequence. The thermal conductivity was carried out in a closed-cycle refrigerator, using a direct heat-pulse technique. Samples were cut to a rectangular parallelepiped shape of typical size $1.5 \times 1.5 \times 5.0$ mm^3 with one end glued (OMEGABOND 200) to a copper block as a heat sink. A calibrated chip resistor (100 Ω at room temperature with size of $1.0 \times 0.5 \times 0.3$ mm^3), which served as a heat source, was glued to the other end. The temperature difference was measured by an E-type differential

thermocouple with junctions thermally attached to two well-separated positions along the sample. The temperature difference was controlled to be less than 1 K to minimize the heat radiation. During measurements the sample space was maintained in a good vacuum (better than 10^{-4} Torr). All experiments were carried out with a warming rate slower than 20 K h^{-1}. In principle, the Seebeck coefficient and thermal conductivity measurements can be performed simultaneously. The reproducibility of S and κ measurements is better than 2%, while the absolute accuracy of κ is approximately 20%, mainly due to the error on the determination of sample dimensions.

3. Results and discussions

3.1. Resistivity

The low-temperature resistivity in these $Al_{70}Pd_{22.5}Re_{7.5}$ quasicrystals has been studied in detail. It was found that they exhibit a metal–insulator (MI) transition at a critical resistivity ratio $\Re_C \sim 13$ [18]. Therefore, the samples investigated in this paper include both metallic and insulating phases of $Al_{70}Pd_{22.5}Re_{7.5}$ quasicrystals. The temperature dependence of the conductivity σ between 10 and 300 K roughly follows a power law, i.e., $\sigma \propto T^\alpha$ with $\alpha \approx 1.0$ for $\Re < 13$ and $\alpha = 1.3$–1.5 for $\Re > 13$ [17].

In figure 1 we show the temperature variation of electrical resistivity for $Al_{70}Pd_{22.5}Re_{7.5}$ quasicrystals with $\Re = 10.2, 19.4, 26.3$ and 84.4, respectively. The values of the resistivity at room temperature are about 90 $\mu\Omega$ m for all samples, and increase with decreasing temperature, exhibiting a semiconductor-like behaviour. Such a non-metallic characteristic and high resistivity value in AlPdRe quasicrystals have been explained by a combination of a Hume Rothery pseudogap in the Fermi level (E_F) density of states (DOS) and localization tendency of electrons near E_F [19]. For metallic samples ($\Re < 13$), the low-temperature $\sigma(T)$ may be manifested by weak localization effects and electron–electron interactions [20], while for insulating samples ($\Re > 13$), the $\sigma(T)$ at low temperatures ($T < 10$ K) can be described well by a variable-range hopping law [19, 21]. However, at high temperatures, the behaviour of $\sigma(T)$ still remains to be understood.

3.2. Seebeck coefficient

The temperature-dependent Seebeck coefficients (S) of $Al_{70}Pd_{22.5}Re_{7.5}$ quasicrystals with various $\Re$ are plotted in figure 2. For the $\Re = 10.2$ and 19.4 samples, the trend of temperature variation in S is rather similar even though the MI boundary has been crossed. In the high-temperature regime, the data show quasilinear behaviour with positive values, signifying that hole-type carriers dominate the high-temperature Seebeck coefficient in these two samples. The S-value at room temperature was found to be +30 μV K^{-1}. With decreasing temperature, S changes sign from positive values to negative values at around 120 K, indicating a change of conduction mechanism or dominant carrier at this temperature. A shallow minimum in Seebeck coefficient was also observed near 70 K. For the large-$\Re$ samples ($\Re = 26.3$ and 84.4) the Seebeck coefficients are positive for the entire temperature range. For the $\Re = 26.3$ sample, a diffusion-like Seebeck coefficient is observed and a small phonon drag peak appears at about 30 K. For $\Re = 84.4$, the Seebeck coefficient increases quasilinearly with rising temperature at low temperatures (below 70 K), and then saturates with a value of about +60 μV K^{-1} at higher temperatures. This value is relatively high compared to those of crystalline and disordered metallic systems. The temperature-dependent Seebeck coefficient in quasicrystals is known to be a strong function of composition and annealing conditions of the sample, as we observed in our $Al_{70}Pd_{22.5}Re_{7.5}$ quasicrystals. Such an unusual $\Re$-dependence on the
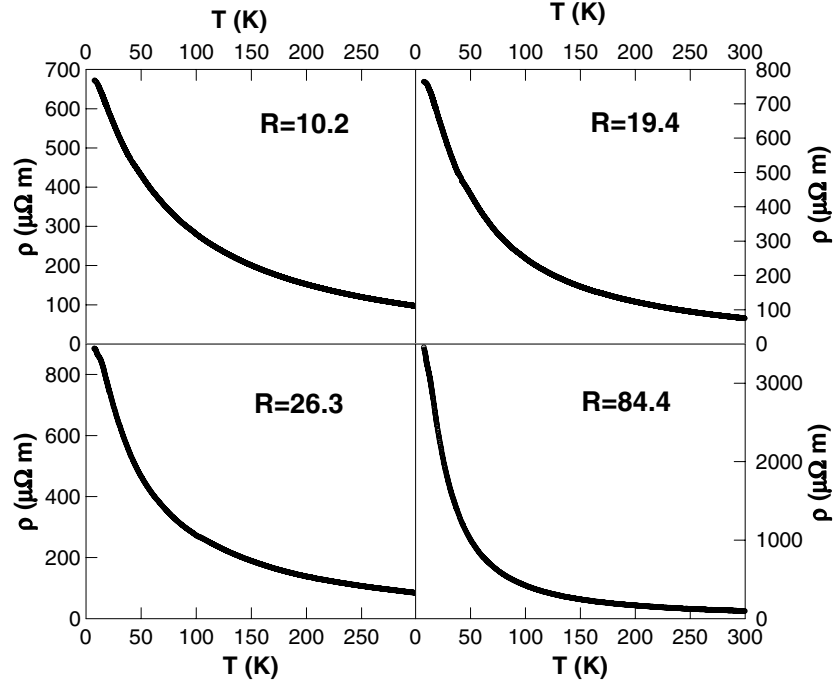
Figure 1. Electrical resistivity as a function of temperature for $Al_{70}Pd_{22.5}Re_{7.5}$ quasicrystals with $\Re = 10.2$, 19.4, 26.3 and 84.4, respectively.

temperature-dependent transport properties of these $Al_{70}Pd_{22.5}Re_{7.5}$ alloys is a reminiscence of semiconducting rather than metallic character.

As the Seebeck coefficient is a sensitive probe of energy relative to the Fermi level E_F, the measured Seebeck coefficient can be used to characterize the band shape around the Fermi surface. Therefore, in the following we try to understand the significant $\Re$-dependence of the Seebeck coefficients for the studied materials with the pseudogap scenario. It is well known that the AlPdRe quasicrystals possess a Hume Rothery pseudogap in the Fermi level DOS [19]. Generally a diffusion-like Seebeck coefficient is observed in these alloys (except $\Re = 84.4$ at high temperatures) as S increases quasilinearly with rising temperature. This characteristic can be described by the classical Mott's formula

$$S_e = \frac{\pi^2 k_B^2}{3e} T \left(\frac{1}{\sigma(E)} \frac{\partial \sigma(E)}{\partial E} \right)_{E=E_F} \propto \left(\frac{1}{N(E)} \frac{\partial N(E)}{\partial E} \right)_{E=E_F}$$

assuming a one-band model with an energy-independent relaxation time, where $\sigma(E)$ is the electrical conductivity and $N(E)$ is the electron DOS. Our measured data show that the room-temperature Seebeck coefficient increases with $\Re$-value. This corresponds to a larger energy derivative of $N(E)$ at Fermi energy for the large-$\Re$ sample, assuming that $N(E)$ has a weaker dependence on the sample than its energy derivative. A larger energy derivative of $N(E)$ indicates a deepening of the pseudogap in the Fermi level DOS. Such a change in band shape around the Fermi surface was proposed previously to justify the composition dependence of the Seebeck coefficients of AlPdRe icosahedral quasicrystals, as illustrated in figure 8 of [12]. For the present case, a sample with larger $\Re$ represents a more pronounced pseudogap feature, consistent with the finding of tunnelling spectroscopy that the spiky pseudogap tends to become
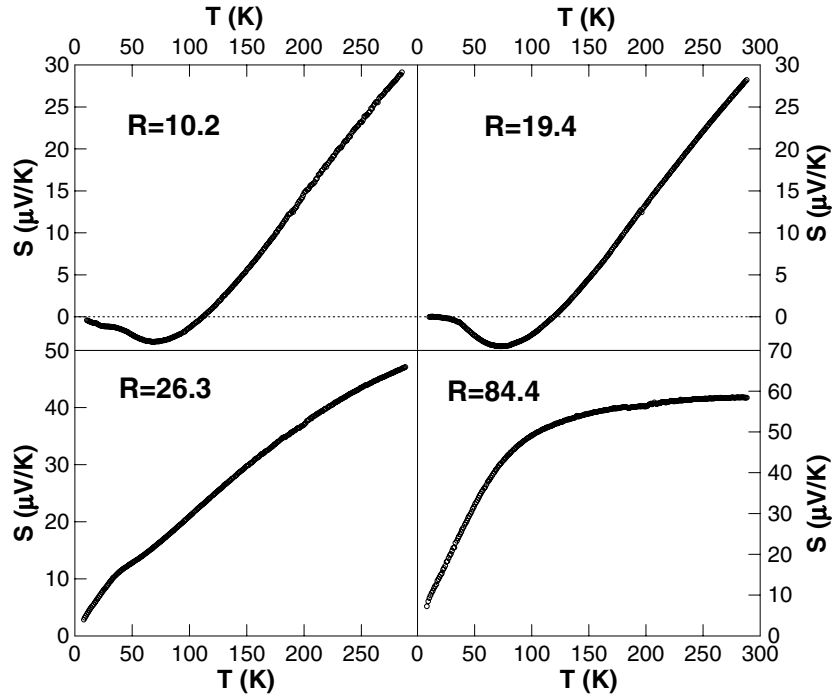
Figure 2. Seebeck coefficient as a function of temperature for Al$_{70}$Pd$_{22.5}$Re$_{7.5}$ quasicrystals with various $\Re$.

narrower as the value of $\Re$ increases [22]. In this regard, the occurrence of a larger energy derivative of $N(E)$ at E_F is expected for a larger-$\Re$ sample, which in turn gives rise to a higher Seebeck coefficient in these materials.

3.3. Thermal conductivity

In figure 3, we show the observed thermal conductivity (κ) for all samples studied. Our measurements indicate that the thermal conductivity in these materials is almost sample independent. The observed thermal conductivity decreases with decreasing temperature until the appearance of a broad minimum at around 120 K and a peak near 30 K, in agreement with the expectation of generalized Umklapp processes in quasicrystals [23]. The pronounced peak in κ is an indication of very high structure perfection of these quasicrystals. The values of κ are observed to be between 1 and 2.5 W m^{-1} K^{-1} in the temperature range we investigated, consistent with the values reported in other icosahedral quasicrystals such as Al$_{72}$Pd$_{19.5}$Mn$_{8.5}$ [24]. Since the thermal conductivity of quasicrystals is expected to closely follow Wiedemann–Franz's law over a wide temperature range [25], the electronic thermal conductivity is estimated by using $\kappa_e \rho / T = L_0$. Here ρ is the dc electric resistivity and the Lorentz number $L_0 = 2.45 \times 10^{-8}$ W Ω K^{-2}. As illustrated in figure 3, the solid lines represent the calculated κ_e for each sample. From this estimation, we clearly demonstrated that the total thermal conductivity is mainly due to lattice phonons rather than charge carriers in these Al$_{70}$Pd$_{22.5}$Re$_{7.5}$ quasicrystals.

Another interesting feature of the thermal conductivity of these quasicrystals is the monotonic increase of the thermal conductivity with increasing temperature above 120 K.
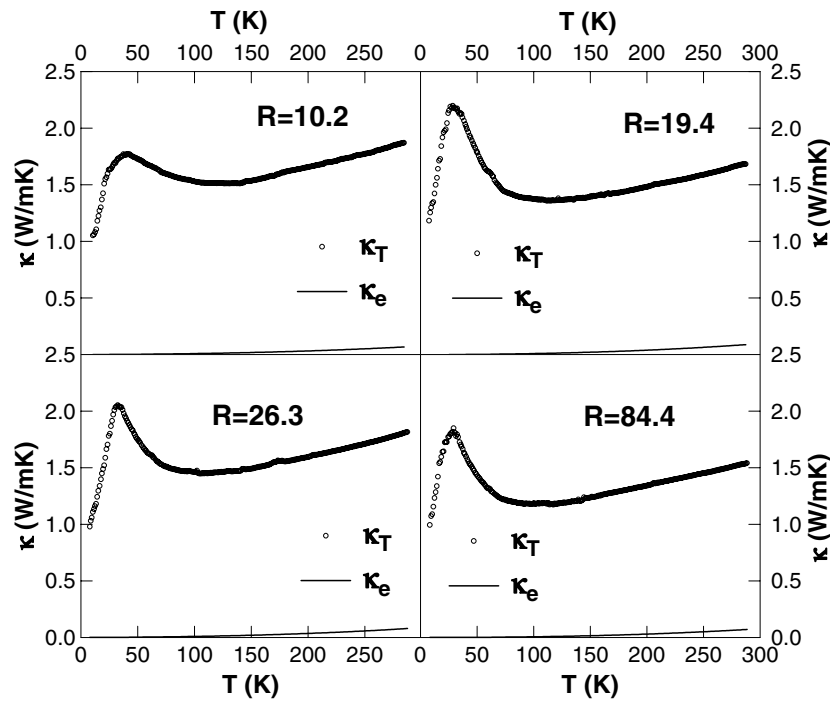
Figure 3. Thermal conductivity as a function of temperature for $Al_{70}Pd_{22.5}Re_{7.5}$ quasicrystals. The solid lines represent the electronic contribution to the total thermal conductivity calculated by Wiedemann–Franz's law.

The increase of thermal conductivity above approximately 100 K is a common feature of all quasicrystals, and is attributed to the activation of localized phonon states at high temperatures. Janot proposed a model taking into account the high energy and localized vibration modes with a hierarchical variable-range hopping mechanism, suggesting that the lattice thermal conductivity follows a power law dependency, i.e. $\kappa_L \propto T^n$ with $n = 1.5$ [26]. To examine the validity of this model for our samples, the data above 150 K were fitted by the expression $\kappa = A + BT^n$. These fitting processes yield $n = 1.38 \pm 0.3$, which is in good agreement with the theoretical prediction [26].

4. Summary

In this paper, we present the measurements of electrical and thermal transport properties on four $Al_{70}Pd_{22.5}Re_{7.5}$ samples with a resistivity ratio $\Re = \rho_{4.2\,K}/\rho_{300\,K}$ ranging from 10.2 to 84.4. Due to the weak localization effect, the resistivity exhibits a semiconductor-like behaviour for all materials studied. The Seebeck coefficient in $Al_{70}Pd_{22.5}Re_{7.5}$ quasicrystals is found to be very sensitive to $\Re$. The strong $\Re$-dependence of the Seebeck coefficient in these alloys could be attributed to a change in the band shape around the Fermi surface, where the electron DOS spectrum for samples with larger $\Re$ has a deepening of the DOS pseudogap. On the other hand, the thermal conductivity values in the $Al_{70}Pd_{22.5}Re_{7.5}$ system are almost unaffected by annealing procedures we currently employed. Lattice phonons rather than charge carriers mainly contribute to the total thermal conductivity in these $Al_{70}Pd_{22.5}Re_{7.5}$ quasicrystals. The thermoelectric figure of merit at room temperature is larger with increasing

$\Re$-value ($ZT \sim 0.01$ for $\Re = 84.4$ sample). However, it is still two orders of magnitude lower than in conventional thermoelectric materials. Even though the high resistive nature of the AlPdRe quasicrystals makes this system not yet suitable for practical thermoelectric applications, the strong dependence of the thermoelectric figure on annealing conditions of the AlPdRe quasicrystals still warrants further investigations on the optimization of their thermoelectric performance.

Acknowledgments

References

[1] For a review article, see Tritt T and Pope A 2001 Overview of the thermoelectric properties of quasicrystalline materials and their potential for thermoelectric applications *Semicond. Semimet.* **70** 77–115 and references therein
[2] Macia E 2000 *Appl. Phys. Lett.* **77** 3045
[3] Macia E 2001 *Phys. Rev.* B **64** 094206
[4] Pope A, Tritt T, Chernikov M and Feuerbacher M 1999 *Appl. Phys. Lett.* **75** 1854
[5] Gianno K, Sologubenko A, Chernikov M, Ott H, Fisher I and Canfield P 2000 *Mater. Sci. Eng.* A **294** 715
[6] Pope A, Schneidmiller R, Kolis J, Tritt T, Gagnon R, Strom-Olsen J and Legault S 2001 *Phys. Rev.* B **63** 052202
[7] Pope A, Tritt T, Gagnon R and Strom-Olsen J 2001 *Appl. Phys. Lett.* **79** 2345
[8] Pope A, Tritt T, Gagnon R, Strom-Olsen J, Legault S, Schneidmiller R and Kolis J 2002 *Mater. Res.* **17** 1814
[9] Bilusic A, Smontara A, Lasjaunias J, Ivkov J and Calvayrac Y 2000 *Mater. Sci. Eng.* A **294** 711
[10] Bilusic A, Pavuna D and Smontara A 2001 *Vacuum* **61** 345
[11] Bilusic A, Budrovic Z, Smontara A, Dolinsek J, Canfield P and Fisher I 2002 *J. Alloys Compounds* **342** 413
[12] Kirihara K and Kimura K 2002 *J. Appl. Phys.* **92** 979
[13] Kirihara K, Nagata T and Kimura K 2002 *J. Alloys Compounds* **342** 469
[14] Muro Y, Sasakawa T, Suemitsu T, Takabatake T, Tamura R and Takeuchi S 2002 *Japan. J. Appl. Phys.* **41** 3787
[15] Honda Y, Edagawa K, Yoshioka A, Hashimoto T and Takeuchi S 1994 *Japan. J. Appl. Phys.* **33** 4929
[16] Poon S J, Zavaliche F and Beeli C 1998 *Mater. Res. Soc. Symp. Proc.* 553
[17] Lin C R, Lin S T, Wang C R, Chou S L, Horng H E, Cheng J M, Yao Y D and Lui S C 1997 *J. Phys.: Condens. Matter* **9** 1509
[18] Wang C-R and Lin S-T 1999 *J. Phys. Soc. Japan* **68** 3988
[19] Kimura K and Takeuchi S 1999 *Quasicrystals: the State of the Art* 2nd edn, ed D P Divincezo and P J Steinhardt (Singapore: World Scientific) p 325
[20] Wang C R, Su T I and Lin S T 2000 *J. Phys. Soc. Japan* **69** 3356
[21] Guo Q and Poon S J 1996 *Phys. Rev.* B **54** 12793
[22] Escudero R, Lasjaunias J C, Calvayrac Y and Boudard M 1999 *J. Phys.: Condens. Matter* **11** 383
[23] Kalugin P, Chernikov M, Bianchi A and Ott H 1996 *Phys. Rev.* B **53** 14145
[24] Bilusic A, Budrovic Z and Smontara A 2001 *Fizika* A **10** 121
[25] Macia E 2002 *Appl. Phys. Lett.* **81** 88
[26] Janot C 1996 *Phys. Rev.* B **53** 181