

Thermal expansion of the disordered conductors $MNiSn$ ($M = Ti, Zr, Hf$)

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(Received 30 June 1994)

We report on the behavior of the low-temperature transport properties and thermal expansion of the intermetallic compounds $MNiSn$ ($M = Ti, Zr, Hf$) through the metal-insulator transition. In the low-conductivity samples [$\sigma \sim 10^2$ ($\Omega \text{ cm}$) $^{-1}$] situated on the metallic side, the conductivity σ varies at $T < 10$ K as $\sigma \approx \sigma_0 + A_0 \sqrt{T}$, which may be ascribed to a Coulomb-interaction correction. For the same temperature interval an anomalous negative thermal expansion with negative values approximately proportional to the degree of interaction, evaluated from the conductivity, was observed. A discussion of the possible effect of electron-electron interaction on the electron thermal expansion based on the results of Altshuler and Aronov is also presented.

Recently, substantial progress has been achieved in the understanding of the properties of disordered electron systems (DES). On the metallic side, far from the metal-insulator (MI) transition, one-electron and interaction effects on the low-temperature asymptotic behavior of the conductivity and the magnetoresistivity were consistently described by theory (for review see Refs. 1 and 2). It has been found by Altshuler and Aronov² (see also Refs. 1, 3, and 4) that in disordered systems the electron-electron interaction effects give rise to the appearance of a singularity in the density of states at the Fermi level E_F (unlike the case of a perfect metal) and, therefore, to a nontrivial temperature dependence of thermodynamic properties.

However, as to the experimental confirmation of these predictions, the situation is far from being clear. The thermodynamic measurements were restricted, to the best of our knowledge, to the specific heat ones and no studies of the thermal expansion of DES have been made. As to the specific heat, the most studied system is Si:P where a deviation of the electronic specific heat from that of an ideal system has been found by Kobayashi *et al.*⁵ and has been afterwards studied in more detail.^{6,7} In these recent studies the main attention is devoted to the contribution to the specific heat of the localized electronic states which are leading in the insulating state of the MI transition.⁸ Some evidence of anomalous excess specific heat near the MI transition was obtained by Mael, Yoshizumi, and Geballe⁹ in their study of amorphous $Mo_x Ge_{1-x}$ thin films. However the anomalous contribution to the specific heat proved to be fairly small at the metallic side and, moreover, it was suspected⁹ to be due to the amorphous structure effects.

In this paper we report the results on the thermal expansion and transport properties of the intermetallic compounds $MNiSn$ ($M = Ti, Zr, Hf$). Our important finding is that on the metallic side of the MI transition we observed the negative thermal expansion which is maximum for the samples where the effects of disorder-

mediated electron-electron interaction are most pronounced as is visible from the temperature dependence of the resistivity.

Polycrystalline $MNiSn$ alloys were prepared by melting together the pure constituents, containing not less than 99.99% of the main component, in an electric-arc furnace in a purified argon atmosphere. The weight losses during arc melting were less than 0.2% of the total mass. The alloys were annealed in quartz cells at 800°C in vacuum for different times for up to 30 days.

The x-ray study of our samples was carried out with DRON2.0 and DRON3.0 apparatus using either Fe $K\alpha$ or Cu $K\alpha$ radiation described previously by Scolozdra, Stadnik, and Starodinova¹³ reveals narrow Bragg peaks indexed quite successfully in a MgAgAs-type cubic crystal structure. The composition and structure of the prepared alloys were also analyzed by the powder method on a HSG-4a diffractometer, using Cu $K\alpha$ radiation. Data analysis was performed using the PMNK program.¹⁴ In our investigations only the samples with diffraction patterns not revealing the presence of other phases were used.

The electric, magnetic, and structural behavior of these materials have been studied before.¹⁰⁻¹² These compounds are nonmagnetic (the magnetic susceptibility $\chi < 10^{-5}$ cm³/g down to $T = 4.2$ K). The presence of diffuse scattering in the x-ray data has been interpreted as being due to intersubstitution between Zr and Sn or Hf and Sn in, correspondingly, the ZrNiSn and HfNiSn compounds and being due to intersubstitution between Ni and Sn in TiNiSn.¹⁰ The level of the intersubstitution was estimated from the best fit in the simulation of the k -space distribution of the diffuse scattering intensity and is described by the fraction x of wrongly occupied sites. For example, for ZrNiSn one can write¹⁰ the chemical formula as $Zr_{1-x}Sn_xNi(\text{Vac})Sn_{1-x}Zr_x$ ($0.1 < x < 0.3$). The more ordered samples ($x < 0.2$) exhibit a semiconductorlike temperature dependence of resistivity R for all

temperatures studied ($0.1 < T < 1000$ K), while the less ordered ($x > 0.2$) show a metallic $R(T)$ behavior for $T < 100$ K. All samples display a semiconductorlike $R(T)$ for $T > 500$ K, which has been interpreted¹⁰ as evidence of a gap of order 0.1–0.2 eV. With changing of the degree of partial disorder (x) the density of the electronic states inside the gap changes and as a result a MI transition occurs in the $M\text{NiSn}$ system.^{10,11} The boundary between the metallic and insulating samples has been defined in Ref. 15 where the dependence $\sigma(4.2\text{ K}) = f[\sigma(250\text{ K})]$ measured for more than 20 samples was plotted and by extrapolating from the linear part of the dependence the so-called minimum metallic conductivity σ_{min} which has been estimated to be about $\sigma_{\text{min}} \sim 70 \pm 10 \Omega^{-1} \text{ cm}^{-1}$. The samples with conductivity at 4.2 K less than σ_{min} have been considered as situated at the insulating side of the MI transition. For our studies we choose five different samples: two ZrNiSn (N.1 and N.2), one HfNiSn (N.3) and two TiNiSn (N.4 and N.5): four of them (N.1–N.4) situated on the metallic side and N.5 on the insulating side of the MI transition.

The thermal expansion measurements were made using the three-terminal capacitance method, as described in Ref. 16. The transport properties (resistivity R , Seebeck coefficient S , thermal conductivity K) were measured simultaneously with the same procedure as described before.¹²

The thermal-expansion coefficient versus temperature of the two studied ZrNiSn samples is presented in Fig. 1. For ZrNiSn N.2, which shows a poor metallic conductivity [$\sigma \geq 10^3 (\Omega \text{ cm})^{-1}$], which masks a possible effect of electron-electron interactions on the conductivity, the thermal expansion below $T \approx 15$ K is rather small, namely, $\alpha < 10^{-8} (1/\text{K})$. A spectacularly different thermal expansion is shown by ZrNiSn N.1 which displays below 20 K a change from positive to negative values with a

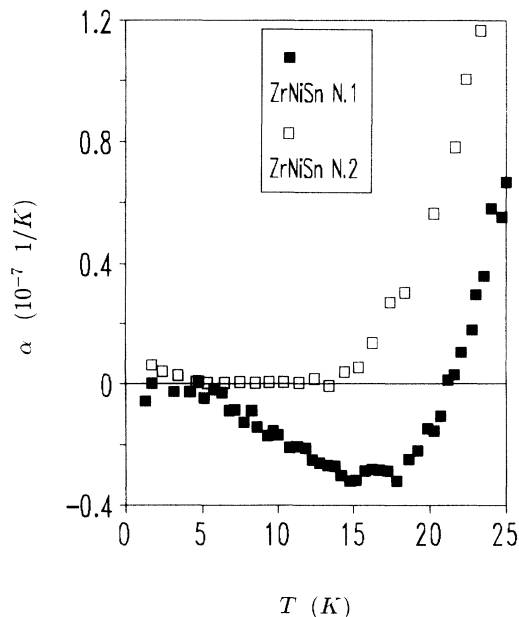


FIG. 1. Temperature dependences of the thermal expansion of the ZrNiSn N.1 and ZrNiSn N.2 samples.

minimum α of about $-0.3 \times 10^{-6} (1/\text{K})$ at $T = 15$ K. In our opinion, this effect cannot originate from the disorder (since it is smaller in the more disordered ZrNiSn sample N.2) nor from an anisotropic polycrystal growth (the lattice symmetry is cubic) or from some kind of spin contribution because all $M\text{NiSn}$ ($M = \text{Ti, Zr, Hf}$) compounds are Pauli paramagnets. Furthermore, the $\alpha(T)$ coefficient of metallic ZrNi_2Sn is positive in the measured temperature range.

Figure 2 shows the temperature dependencies of $R(T)$, $S(T)$, and $K(T)$ for ZrNiSn N.1. The pronounced maximum of $K(T)$ with T_{max} at about 40 K suggests an almost regular lattice structure. The small values of the Seebeck coefficient and quasimetallic $R(T)$ behavior at $25 < T < 70$ K indicate^{10,12} that ZrNiSn N.1 is close to the

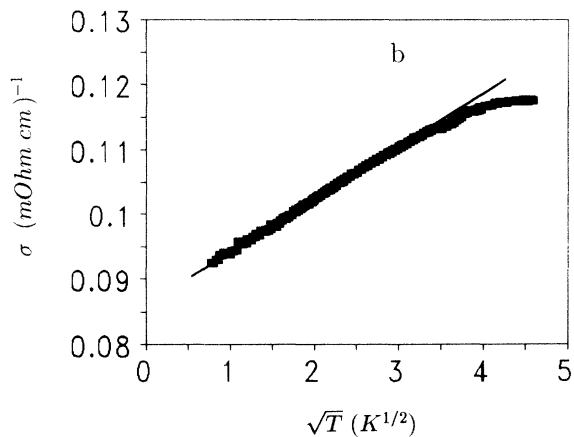
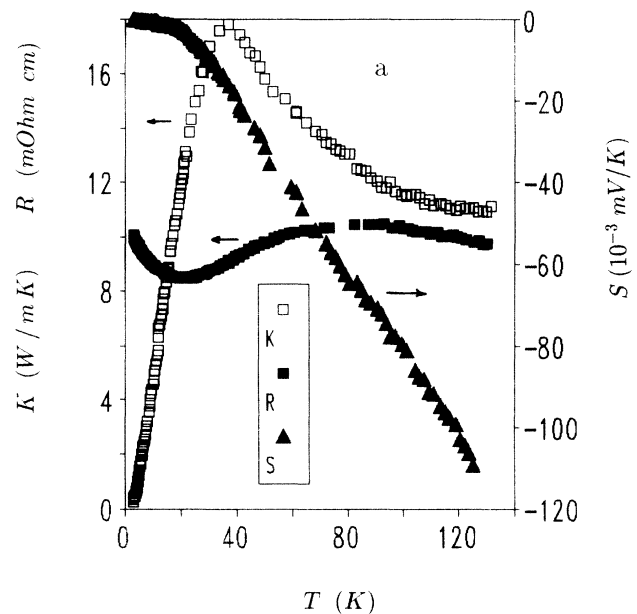


FIG. 2. (a) Temperature dependences of the resistivity R , thermal conductivity K , and Seebeck coefficient S for ZrNiSn N.1. Graph (b) presents a plot of $R^{-1} = \sigma(T)$ vs \sqrt{T} of the same sample in the low-temperature region. The solid line corresponds to the least-squares fit.

MI transition from the metallic side. This becomes more evident when one plots the conductivity σ vs \sqrt{T} (see lower part on Fig. 2). The excellent fit of our data for ZrNiSn N.1 to a straight line $\sigma \propto \sqrt{T}$ within the range of 0.58–9 K implies that Coulomb interactions between electrons have a dominating effect on the conductivity in agreement with the theory.² Some negligible deviation between 4 and 9 K from the line (of less than 1%) may be due to the localization effects. Note that the value of the coefficient A_0 in the asymptotic regime ($T \rightarrow 0$), $\sigma \approx \sigma_0 + A_0\sqrt{T}$ ($A_0 = 7.9 \text{ } \Omega^{-1} \text{ cm}^{-1} \text{ K}^{-1/2}$) is significantly higher than those reported before for other disordered and amorphous metals^{1,2} or quasicrystals.¹⁷

Figure 3 presents the temperature dependencies of the thermal expansion for TiNiSn and HfNiSn. For TiNiSn an $\alpha(T)$ behavior close to the one observed for ZrNiSn N.1 was obtained. At the same time the HfNiSn sample shows a less dramatic, but clear inversion of α below $T \approx 14$ K. For both samples, the asymptotic behavior $\sigma \approx \sigma_0 + A_0\sqrt{T}$ was observed below $T \approx 10$ K. For TiNiSn the ratio A_0/σ_0 was found to be about 1.5 times higher; for HfNiSn, about four times smaller than that for ZrNiSn N.1. For the TiNiSn N.5 with $\sigma_0 \sim 5 \text{ } \Omega^{-1} \text{ cm}^{-1}$ much less than the minimum metallic conductivity σ_{\min} the negative thermal expansion effect disappears (see Fig. 3).

Thus, our experimental data indicate a relationship between the negative thermal expansion and the character of electron transport in the studied materials. To show it more clearly we have plotted in Fig. 4 the dependence of the minimum value of the thermal expansion in the temperature interval $10 < T < 20$ K, α_{\min} , as a function of the corresponding A_0 coefficient. We suggest that the increase of $|\alpha_{\min}|$ as a function of A_0 reflects the importance of the electron-electron correlations. The plot in

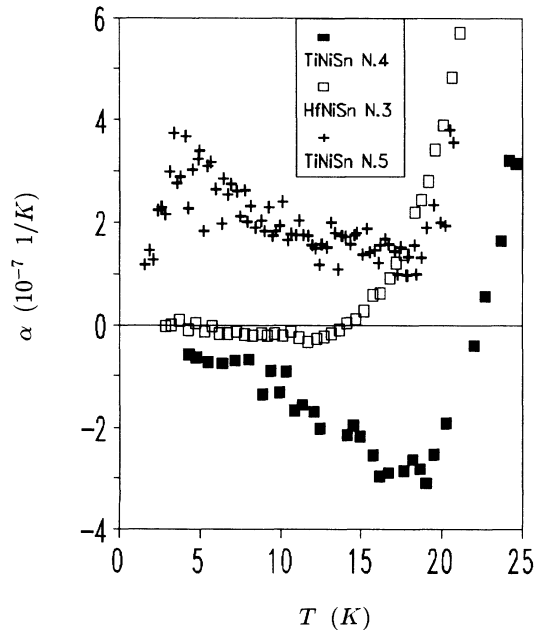


FIG. 3. Temperature dependences of $\alpha(T)$ for HfNiSn N.3, for TiNiSn N.4 and N.5.

Fig. 4(b) emphasizes the transformation of the low-temperature thermal expansion through the metal-insulator transition: α_{\min} is small in the metallic side far from the MI transition, shows maximum absolute values on the metallic side for $\sigma \sim \sigma_{\min}$, decreases rapidly when moving into the insulating side near σ_{\min} , and is small and positive on the insulating side where localized electron states may play a dominating role.

The negative electronic thermal expansion in metals is associated usually with a nontrivial band structure at the Fermi energy: several bands are generally necessary to describe the experimental results.^{18–20} In our case, however, the negative region were the localization effects are visible in the temperature dependence of conductivity. This implies an involvement into the phenomenon of the influence of disorder on the low-temperature thermodynamic properties of the electron subsystem. Keeping

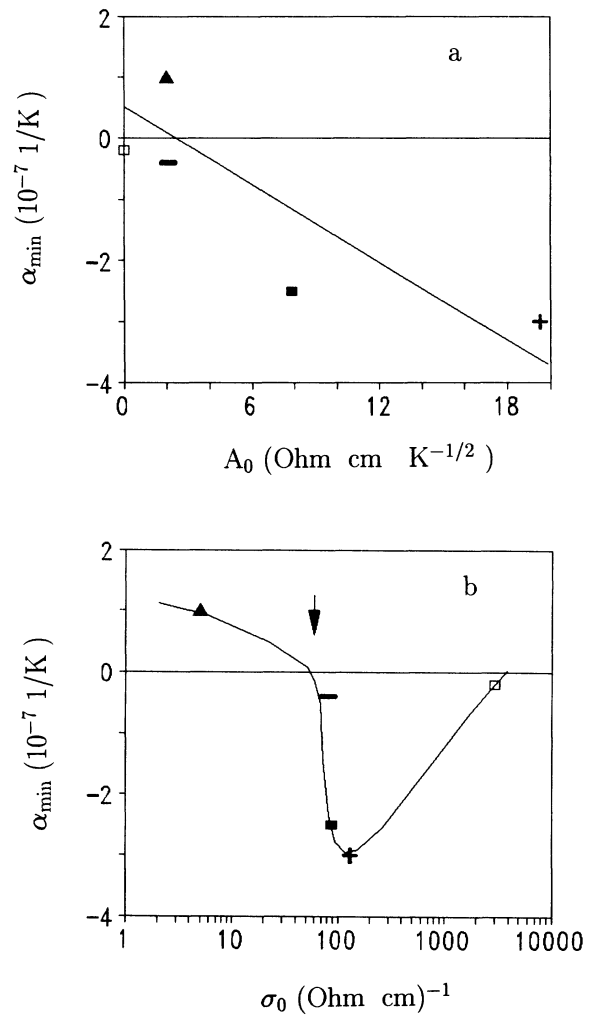


FIG. 4. (a) Dependence of the α_{\min} (see text) on the A_0 coefficient for ZrNiSn N.1 (■), ZrNiSn N.2 (□), HfNiSn N.3 (▲), TiNiSn N.4 (+), and TiNiSn N.5 (▼). (b) Dependence of α_{\min} on σ_0 . Lines are a guide for the eyes and arrow shows the σ_{\min} (i.e., MI transition) position.

in mind the qualitative character of the discussion which follows we adduce only the part of the interaction contribution, that in the so-called diffusion channel,²

$$\Delta S = \left(\frac{2}{3} - \frac{3}{2}F\right)\xi \left(\frac{T}{D\hbar}\right)^{3/2} V, \quad (1)$$

where S is the entropy, D is the diffusion coefficient, F is an electron-electron interaction characteristic of Fermi liquid (see below and Ref. 2), and $\xi \approx 10^{-2}$. Equation (1) is valid, strictly speaking, only at $F \ll 1$, but qualitatively its form remains the same even when this condition is not fulfilled. Using the Maxwell relation one has for the thermal expansion coefficient α ,

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p = k \left(\frac{\partial S}{\partial V}\right)_T, \quad (2)$$

where p is pressure.

We now have to analyze the V dependence of the parameters entering in Eq. (1). Let us begin with D . Neglecting, within our qualitative analysis, the electron-electron interaction contribution to D one has

$$D \propto \frac{E_F \tau}{m} \propto \frac{E_F}{m^2 p_F n} \propto \frac{p_F}{m^3 n}, \quad (3)$$

where τ is the collision time, n is the concentration of scattering centers, p_F is the Fermi momentum, and m is the effective mass. As $p_F \propto V^{-1/3}$ and $n \propto V^{-1}$ one sees that

$$D \propto \frac{V^{2/3}}{m^3(V)}. \quad (4)$$

So, it is easy to see from Eqs. (4) and (1) that, if the V dependence of F and m is neglected, then the electron-electron interaction modified by disorder gives no contribution to the thermal expansion.

Taking into account the V dependence of the parameter of electron-electron interaction F , we restrict ourselves to the simplest case when the inverse screening length $\kappa = \sqrt{(4e^2 m p_F)/\pi}$ is much smaller than p_F (here e is the electron charge). In this case

$$F = \frac{\kappa^2}{2p_F^2} \propto \frac{m}{p_F}. \quad (5)$$

We see that if m does not depend on V , then $F \propto V^{1/3}$

and one obtains a negative value of α . The V dependence of m (we assume that $m'_V > 0$) provides both positive and negative contributions. The first is due to the m dependence of the diffusion coefficient D and the second is due to the m dependence of F . Thus, it seems to be quite realistic to consider the negative contribution to the thermal-expansion coefficient as that due to the disorder-modified electron-electron interaction. Let us mention as well that the contribution to the thermal expansion of isolated spin states⁸ is positive if the characteristic radius of the exchange interaction does not have an exotic V dependence.

In conclusion we have observed the negative thermal expansion of $M\text{NiSn}$ ($M = \text{Ti, Zr, Hf}$) compounds which is maximum in the absolute value for the samples where the effects of disorder mediated electron-electron interaction are most pronounced as is visible from temperature dependence of the resistivity. Let us discuss why the systems investigated may provide better conditions for the observation of the electron-electron interaction effects than those previously studied. First, unlike $\text{Mo}_x\text{Ge}_{1-x}$ samples⁹ they have fairly perfect crystalline structure (narrow Bragg peaks), i.e., the intersubstitution between atoms may be considered as mainly electronic but not as a structural defect and thus the effects specific for amorphous dielectric structures are not expected to play a role in our case. Second, the electron concentration¹⁰ $n_e \approx 10^{20} - 10^{21} \text{ cm}^{-3}$ is much higher in our case than for Si:P and, therefore, the electronic contribution to the thermodynamic parameters as a whole, is much bigger. Third, it may be a matter of chance that the electron effective mass depends very weakly on V in the systems studied or there might be other, still unrevealed, specific features of the V dependence of the material constants involved which lead to the strong negative contribution to the thermal expansion coefficient of the electron-electron interactions.

We would like to acknowledge V. V. Pryadun and A. Leventsov for help in our experiments as well as N. B. Brandt, I. P. Zviagin, and J. M. Calleja for discussion. F.G.A. and A.P.L. gratefully acknowledge financial support from the Universidad Autonoma de Madrid and the Ministry of Science and Education of Spain. The experimental work was supported by Grant No. MAT92-0170 from Plan Nacional de Materiales.

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¹P. A. Lee and T. V. Ramakrishnan, *Rev. Mod. Phys.* **57**, 287 (1985).

²B. Altshuler and A. Aronov, in *Electron-Electron Interactions in Disordered Systems*, edited by A. Efros and M. Pollak (North-Holland, Amsterdam, 1985).

³B. L. Altshuler and A. G. Aronov, *Zh. Eksp. Teor. Fiz.* **77**, 2028 (1979) [*Sov. Phys. JETP* **50**, 968 (1979)].

⁴B. L. Altshuler and A. G. Aronov, *Solid State Commun.* **30**, 115 (1979).

⁵N. Kobayashi, S. Ikehata, S. Kobayashi, and W. Sasaki, *Solid*

State Commun. **32**, 1147 (1979).

⁶M. A. Paalanen, J. E. Graebner, R. N. Bhatt, and S. Sachdev, *Phys. Rev. Lett.* **61**, 597 (1988).

⁷M. Lakner and H. V. Lohneysen, *Phys. Rev. Lett.* **63**, 648 (1989).

⁸R. N. Bhatt and D. S. Fisher, *Phys. Rev. Lett.* **68**, 3072 (1992).

⁹D. Mael, S. Yoshizumi, and T. H. Geballe, *Phys. Rev. B* **34**, 467 (1986).

¹⁰F. G. Aliev, N. B. Brandt, V. V. Moshchalkov, V. V. Kozrykov, R. V. Scolozdra, and A. I. Belogorokhov, *Z. Phys. B* **75**, 167 (1989).

- ¹¹F. G. Aliev, V. V. Kozyrkov, V. V. Moshchalkov, R. V. Scolozdra, and K. Durczewski, *Z. Phys. B* **80**, 353 (1990).
- ¹²F. G. Aliev, *Physica B* **171**, 199 (1991).
- ¹³R. V. Scolozdra, Yu. V. Stadnik, and E. E. Starodinova, *Ukr. Fiz. Zh.* **31**, 1258 (1986) [*Ukr. Phys. J* **31**, 720 (1986)].
- ¹⁴V. K. Pecharskii, P. Yu. Zavalii, L. G. Akselrud, Yu. N. Grin, and E. I. Gladushevskii, *Bull. Lvov State Univ. Chem.* **25**, 9 (1984).
- ¹⁵F. G. Aliev, N. B. Brandt, V. V. Kozyrkov, V. V. Moshchalkov, R. V. Scolozdra, and Yu. V. Stadnik, *Fiz. Nizk. Temp.* **13**, 498 (1987) [*Sov. J. Low Temp. Phys.* **12**, 281 (1987)].
- ¹⁶R. Villar, M. Hortal, and S. Vieira, *Rev. Sci. Instrum.* **51**, 27 (1980).
- ¹⁷M. A. Chernikov, A. Bernasconi, C. Beeli, and H. R. Ott, *Europhys. Lett.* **21**, 767 (1993).
- ¹⁸J. H. O. Varley, *Proc. R. Soc. London Ser. A* **237**, 413 (1956).
- ¹⁹E. P. Fetisov and D. I. Khomski, *Solid State Commun.* **56**, 403 (1985).
- ²⁰C. Bastide and C. Lacroix, *Solid State Commun.* **59**, 121 (1986).