Evidence for Variable Range Hopping Conductivity in the Ordered Quasicrystal *i*-AlPdRe

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We show that the conductivity of the quasicrystal *i*-AlPdRe follows a Mott's variable range hopping conduction law $\sigma(T) = \sigma_0 \exp -(T_0/T)^{1/4}$ in the temperature range 20–600 mK. The *i*-AlPdRe phase thus behaves like disordered insulators at very low temperature. We find a very low activation term $T_0 \sim 1$ mK, which is an indication of a large localization length ξ, in accordance with the vicinity to the metal-insulator transition. This is the first time that a pure Mott's law is observed at very low temperature in a structurally ordered compound made of metallic elements. [S0031-9007(98)07567-X]

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One of the most outstanding properties of quasicrystals is a very low electrical conductivity σ close to the metal-insulator transition (MIT) [1,2]. However, there is no evidence for a gap as in semiconductors, and the structure is highly ordered, although it is nonperiodic. This is unlike Anderson insulators where disorder is the reason for a localization of the electronic wave function.

In the *i*-AlPdRe icosahedral phase, which gives the lowest conducting quasicrystalline samples, even the actual conductivity behavior $\sigma(T)$ is debated. Indeed, extrapolations of $\sigma(T)$ from above 0.45 K [3,4] have suggested a zero conductivity at zero temperature. On the contrary, measurements [5–7] at lower temperatures indicate a saturation of $\sigma(T)$ to a finite value. So the question is still open as to whether the *i*-AlPdRe phase can become a zero temperature insulator. Moreover, the transport properties happen to be very sample dependent [3–10], but it was noted [4,8] that the low conducting *i*-AlPdRe samples present a number of transport properties similar to Mott-Anderson insulators close to the MIT but still on the insulating side, in particular as testified by the magnitude of the conductivity σ, the amplitude of its temperature dependence $R = \sigma_{300\text{-K}}/\sigma_{4\text{-K}}$, the breakdown of weak localization effects as the conductivity decreases [9], and the onset of a correlation gap in the density of states [10].

For Mott-Anderson insulators, conduction at very low temperature proceeds via electron hopping between exponentially localized states. In the mechanism of variable range hopping (VRH) proposed by Mott [11], electrons may preferentially hop to localized sites which are close in energy, but not necessarily close spatially. The conduction law of VRH is given by Eq. (1) of Ref. [11]:

$$\sigma(T) = \sigma_0 \exp -(T_0/T)^p, \qquad (1)$$

with $p = 1/4$. The activation temperature T_0 varies as $1/\xi^3$ where the localization length ξ diverges at the MIT. The widely studied VRH conduction mechanism has been observed at low temperature in many disordered insulators including highly doped semiconductors, semiconductor-metal or insulator-metal alloys [12].

For quasiperiodic structures, there is a strong theoretical background supporting low conducting properties. Numerical simulations on large quasicrystal approximants confirm low conductivity within the Bloch-Boltzman theory, by the prediction of low dispersing bands [13]. In perfect quasiperiodic lattices, the specific electronic wave functions tend to be localized [14] like the critical states (neither exponentially localized as in the Anderson localization, nor extended) and the energy level statistics can be well described by the random matrix theory usually applied to disordered systems [15]. In those model calculations, the electronic propagation is neither ballistic as in the case of periodic systems nor diffusive as for disordered systems. The role of defect or of electron-electron interaction also appears nonconventional [16]. Depending on the energy and the Hamiltonian parameters, the conductivity may increase upon disorder or unexpectedly decrease [17].

In order to understand the mechanism of electronic propagation in the low conducting quasicrystals, there is a need to first clarify the conductivity behavior. The purpose of this paper is to present conductivity measurements at very low temperatures for well characterized *i*-AlPdRe samples. We show for the first time that the conductivity measured down to 20 mK obeys a true VRH law as in disordered insulators, which tends to support a zero conductivity at zero temperature in *i*-AlPdRe.

Samples were prepared as described elsewhere [18]. Ingots of nominal composition $Al_{70.5}Pd_{21}Re_{8.5}$ prepared in an arc furnace were melt-spun and subsequently annealed at high temperature (between 900 and 1010 °C). Samples consist entirely of the high structural quality polygrained *i*-phase, with typical grain size of a few μm, as shown by the sharpness of x-ray diffraction peaks, by transmission and scanning electron microscopy, and by microprobe analysis [18]. A few spots of a secondary AlRe phase were, however, observed, located only at the surface, with a surface fraction of $\sim$3% and $\sim$8% on the smooth and the rough side of the ribbons, respectively. The resistivity $\rho = 1/\sigma$ was measured in the four probe configuration for three samples of slightly different σ values. The

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silver paint electrical contacts were done on the rough and smooth side for sample 1 ($\sigma_{4\text{-K}} \sim 1.4\ (\Omega\ \text{cm})^{-1}$, $R = 128$) and sample 2 [$\sigma_{4\text{-K}} \sim 1.4\ (\Omega\ \text{cm})^{-1}$, $R = 117$], respectively. Sample 3 [$\sigma_{4\text{-K}} \sim 2.5\ (\Omega\ \text{cm})^{-1}$, $R = 84$] was measured on the rough side polished with diamond paste in order to remove the more possible secondary phase. We note the correlation of the low σ values with the strong negative temperature dependencies, as shown by the large R values, as already pointed out in i-AlPdRe for a wider conductivity range [6,8]. Because of the rather poor accuracy in the absolute σ value, $\Delta\sigma \sim \pm(10\text{–}20)\%$, we characterize the samples by the conductivity ratio R.

Measurements were performed with an ac bridge. To ensure a good thermalization of the sample, the ribbons were glued on a massive copper block and insulated by a 10 μm kapton foil with stycast epoxy 1266. Nevertheless, there were clear manifestations of insufficient thermalization below 15 mK, and great care was taken to wait long enough (about 15 min at 30 mK) after the temperature stabilization of the refrigerator, due to the increase of sample thermal response time at low temperature. It stems for the large nuclear hyperfine specific heat [19] together with a long [20] internal response time (the NMR relaxation rate of the nuclei T_1 at very low T) and large thermal resistance between the sample and the sample holder. No self-heating of the sample by the injection current was observed.

In Fig. 1, we present the normalized conductivity $\sigma(T)/\sigma_{1\text{-K}}$. Above about 10 K (not shown here), the conductivity follows a power law temperature dependence $T^{1.5}$ [8]. In the low temperature range, the conductivity decreases smoothly down to ~0.5 K (saturation region), then sharply drops as T tends to zero. This makes clear that by measuring $\sigma(T)$ in the saturation region, the extrapolation to zero temperature gives a finite σ value. It was already noted [18] that the less conductive the sample, the wider the saturation region, which is opposite to what could be expected for a saturation stemming from any secondary metallic phase. We point out that the same trend was observed in disordered InO_x on the insulating side of the transition [21] very close to the MIT. In that case, the saturation was interpreted [21] as the crossover between a high temperature regime, where extended states contribute, and the VRH conduction which is observed at low temperature.

The $\ln\sigma(T)$ versus $T^{-1/4}$ plot presented in Fig. 2 directly shows that the VRH law [i.e., Eq. (1) with $p = 1/4$] fits very well $\sigma(T)$ from 20 to 600 mK. The $\sigma(T)$ data are normalized at 600 mK for clarity. From the linear plot of Fig. 2, we extract for each sample the activation temperature T_0 reported in Table I (fit 1). For all three samples T_0 is very small ($T_0 \sim 1$ mK), which is discussed below. The σ_0 values are of the order of 1 $(\Omega\ \text{cm})^{-1}$ which is quite reasonable in view of the $\sigma_{4\text{-K}}$ values. However, because the absolute σ value is determined only within $\pm(10\text{–}20)\%$, so is σ_0. We have also tried power law fits $\sigma(T) = \sigma_0 + \sigma_1 T^{\alpha}$, which are usually observed with $\alpha = 1/2$ on the metallic side of the MIT. None of these could fit the data. To more accurately show the VRH law, we plot in Fig. 3, $l(T) = \ln(d\ln\sigma/d\ln T)$ which is found to be linear with $\ln T$ (fit 2) in the range 20–600 mK. Following Eq. (1), we indeed have $l(T) = A - p\ln T$ ($A = \text{const}$). In Table I, the extracted values of p are very close to the exponent $1/4$ of the VRH law. The T_0 values are similar to the ones obtained by setting $p = 1/4$ (fit 1).

We also took into account possible temperature dependence of σ_0 of the form [11] $\sigma_0 = AT^{-s}$. Indeed, as the variation $\exp -(T_0/T)^p$ becomes small because $T > T_0$, the temperature dependence of σ_0 may be no more negligible [22]. Following Shafarman [22], we fitted in the inset of Fig. 3 $\delta = d\ln\sigma/d\ln(1/T)$ as a function of $T^{-1/4}$ [From Eq. (1) $\delta = s - p(T_0/T)^p$.] By restricting our analysis to the case $p = 1/4$, we found values of s almost equal to zero, and T_0 values very close to the case of

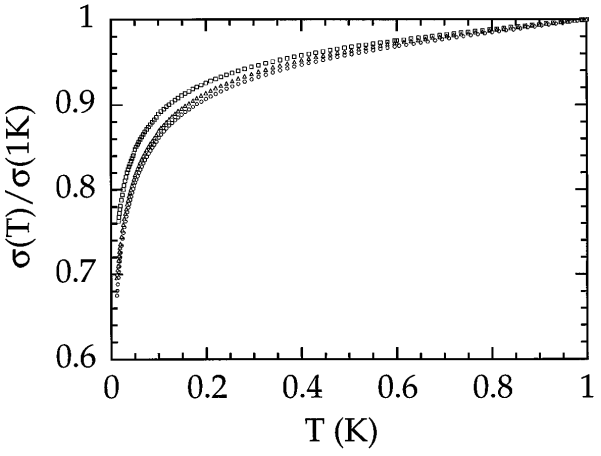

FIG. 1. Conductivity normalized at 1 K for samples 3, 2, and 1 (from top to bottom) in the temperature range 20 mK–1 K.

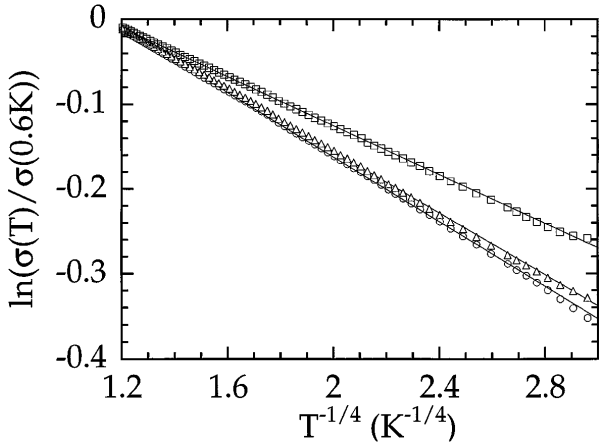

FIG. 2. $\ln\sigma(T)$ versus $T^{-1/4}$ for samples 3, 2, and 1 (from top to bottom) (Fit 1).

TABLE I. Parameters of the VRH conduction $\sigma(T) = \sigma_0 \exp -(T_0/T)^p$ for the three i-AlPdRe samples, following different fit procedures (see text).

	Fit 1 ($p = 1/4, s = 0$)		Fit 2 ($s = 0$)		Fit 3 ($p = 1/4$)	
Samples	T_0 (mK)	$\sigma_0(\Omega^{-1}\ \mathrm{cm}^{-1})$	T_0 (mK)	p	T_0 (mK)	s
Sample 1, $R = 128$	1.31 ± 0.01	1.3	1.4 ± 0.2	0.28 ± 0.01	2.3 ± 0.3	0.013 ± 0.004
Sample 2, $R = 117$	1.10 ± 0.01	1.3	1.0 ± 0.2	0.26 ± 0.01	1.3 ± 0.2	0.005 ± 0.002
Sample 3, $R = 84$	0.455 ± 0.003	2.2	0.39 ± 0.07	0.25 ± 0.01	0.41 ± 0.09	0.000 ± 0.003

fits 1 and 2 (see Table I). We, however, cannot rule out a more complex two-parameter fit.

Finally, we also considered the scattering on dilute magnetic impurities as a possible mechanism for the decrease of σ with temperature. There is no reasonable temperature range, where a $\ln T$ or even a $-T^2$ dependence of $\rho(T) = 1/\sigma(T)$ could be found, as would be expected for a Kondo effect [23]. The curvature of the $\rho(T)$ dependence would indicate a small Kondo temperature T_K ($T_K < 20$ mK) and a low impurity concentration. Moreover in the impurity limit for a metal [23], the increase in $\Delta\rho$ per impurity is very small ($\Delta\rho \sim$ a few $10^{-6}\ \Omega$ cm) compared to the present data. However, one cannot completely rule out a nonusual Kondo effect in relation with the expected complicated electronic density of states of quasicrystals.

From the above analysis, we conclude that the VRH law $\sigma(T) = \sigma_0 \exp -(T_0/T)^{1/4}$ provides the best fit to our data. Following the usual interpretation of this activation law [11,12], we can estimate a localization length ξ from $T_0 \simeq 18/\xi^3 k_B n(E_F)$, where $n(E_F)$ is the electronic density of states at the Fermi level. By using a rough estimate of $n(E_F)$ as obtained from the linear term of specific heat: $C_p(T) = \gamma T$ with $\gamma = 0.1\ \mathrm{mJ/mol\,K^2}$ [3,4,19], we find $\xi \sim 3000$ Å. This is much larger than previous estimates ($\xi \sim 70$ Å and $\xi \sim 30$ Å) for i-AlPdRe phases [3,5], but in these cases an additional conductivity term was necessary to fit the data. Note that $n(E_F)$ is not precisely known in i-AlPdRe, since

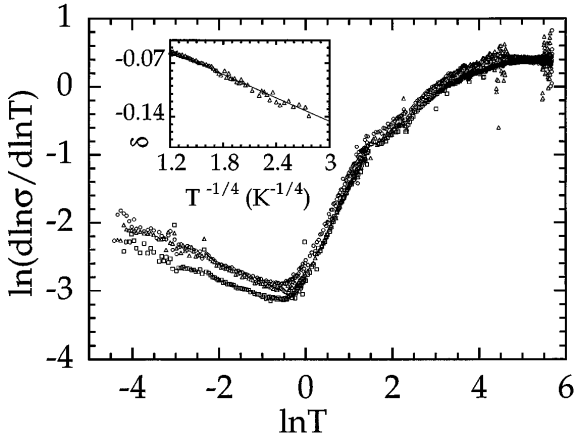

FIG. 3. $l(T) = \ln(d\ln\sigma/d\ln T)$ as a function of $\ln T$ (fit 2) for the three i-AlPdRe samples. Inset: $\delta = d\ln\sigma/d\ln(1/T)$ as a function of $T^{-1/4}$ (fit 3) for sample 2 (see text).

the small γ term is overcome at low temperatures by a strong nuclear hyperfine term [19], and may also contain contributions from two-level systems [19]. If the actual $n(E_F)$ is lowered, ξ would be even larger.

Let us emphasize that the three samples behave similarly, which indicates that the spots of secondary phases have minor influence on the conductivity. Moreover, the T_0, p, and s parameters extracted from the different fits vary all monotonously with R, which in turns appears as a good scaling parameter for the transport properties, as already pointed out for insulating Si:As for instance [22]. In particular, the less conducting the sample (the higher R) the higher T_0, as expected in the VRH mechanism.

We now comment on the VRH law found in i-AlPdRe in comparison with disordered systems. First, it was shown in disordered insulators [12] that the exponent $p = 1/4$ becomes one half by taking into account electron-electron interactions. However, this is only observable [22] for $T < T_0/2000$, which is far from experimental range with $T_0 \sim 1$ mK. The second point concerns the general validity of the VRH law in a temperature region well above T_0. This regime indeed corresponds to the case where the hopping distance defined as [11] $r_{\mathrm{hop}} \simeq 0.4\xi(T_0/T)^{1/4}$ becomes smaller than ξ. Mott's calculation is valid only in the dilute case when localized states are far apart, i.e., $r_{\mathrm{hop}} \gg \xi$. In our case we have estimated $\xi \sim 3000$ Å whereas r_{hop} is only ~600 Å at 20 mK. This problem was already discussed in disordered insulators, close to the MIT. In that case [22], corrections to the Mott's calculation gave the same exponential dependence of the conductivity ($p = 1/4$), and only the preexponential factor $\sigma_0(T)$ was affected. In this regime, correlated many-electron hoppings were also proposed to be significant.

Third, the T_0 values found in the present study are, to our knowledge, among the smallest ever reported. They are consistent with electronic properties, like the σ and R values, very similar to those of insulators close to the MIT. To further study the MIT in i-AlPdRe, one challenge will be to find a physical parameter to monitor the transition, like the carrier density n in doped semiconductors or the metal concentration in semiconductor-metal alloys, since neither the density of states $n(E_F)$ nor the average carrier density, as deduced by the Hall effect, are accurately known. From our study, it seems that R could be a good working parameter. At the microscopic scale, we propose that local composition fluctuations, such as those

estimated by microprobe analysis in our samples (of the order of ~ 1 at. % or less) [18], or variation in the local order, could yield to more or less microscopically insulating regions, and, consequently, to a variety of macroscopic conductivities.

Finally, a straightforward consequence of the observed VRH conduction law is that its extrapolation indicates a zero conductivity at zero temperature, which is further pointing to an insulating behavior in i-AlPdRe, although it is not yet fully understood.

The physical origin of VRH conduction in an atomically ordered quasiperiodic compound is now a challenging question. Indeed, exponentially localized wave functions, as in disordered insulators, have not been found in theoretical calculations for quasicrystals. In Anderson insulator theories, the finding of the VRH law in the macroscopic conductivity is derived from a disordered distribution of microscopic conductances [12]. The finding in perfect quasiperiodic model structures of features resembling those of disordered systems, like localized states—but with a power law decay [14]—or the use of random matrix theory for the energy level spacing description [15] could be invoked to quantitatively understand the present data. Also the unconventional effect of disorder could be considered. For instance, in 3D quasiperiodic lattices including disorder, the quantum diffusion evolves with time from a nonballistic regime to a diffusive regime as in disordered system [17] at long time. At very low temperature one expects to be in a regime of long inelastic scattering time, and following these authors, in a regime of diffusive propagation, that could hence yield Anderson transition. Note that a diffusive regime was inferred from magnetoresistance analysis in samples on the metallic side of the MIT [9]. As a final remark, because of the T_0 value being so low, the i-AlPdRe system also opens new possibilities to study the critical regime very close to the MIT, where data are still lacking.

In summary, we have presented evidence for a low temperature variable range hopping conduction in the quasicrystalline i-AlPdRe. The activation temperature T_0 is found to be extremely low ($T_0 \sim 1$ mK), corresponding to a large localization length ($\xi \sim 3000$ Å). This is the first time that a pure VRH law is observed in a structurally ordered compound made of metallic elements.

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[1] S. J. Poon, Adv. Phys. **41**, 303 (1992).
[2] T. Klein, C. Berger, D. Mayou, and F. Cyrot-Lackmann, Phys. Rev. Lett. **66**, 2907 (1991).
[3] Q. Guo and S. J. Poon, Phys. Rev. B **54**, 12 793 (1996).
[4] F. S. Pierce, Q. Guo, and S. J. Poon, Phys. Rev. Lett. **73**, 2220 (1994).
[5] C. R. Wang, C. R. Lin, and S. T. Lin, in *Proceedings of the International Conference ICQ6*, edited by S. Takeuchi and T. Fujiwara (World Scientific, Singapore, 1997), p. 583.
[6] M. Ahlgren, C. Gignoux, M. Rodmar, C. Berger, and Ö. Rapp, Phys. Rev. B **55**, R11 915 (1997).
[7] A. Bianchi, F. Bommeli, M. A. Chernikov, U. Gubler, L. Degiorgi, and H. R. Ott, Phys. Rev. B **55**, 5730 (1997); Y. Honda, K. Edagawa, A. Yoshioka, T. Hashimoto, and S. TakeuchI, Jpn. J. Appl. Phys. **33**, 4929 (1994).
[8] C. Gignoux, C. Berger, G. Fourcaudot, J. C. Grieco, and H. Rakoto, Europhys. Lett. **39**, 171 (1997).
[9] M. Ahlgren, M. Rodmar, C. Gignoux, C. Berger, and Ö. Rapp, Mater. Sci. Eng. **A226–A228**, 981 (1997).
[10] T. Schaub *et al.*, in Proceedings of the 10th International Conference on Liquid and Amorphous Metals, Dortmunt, 1998 (to be published); C. R. Lin, S. L. Chou, and S. T. Lin, J. Phys. C **8**, L725 (1996).
[11] N. F. Mott, J. Non-Cryst. Solids **1**, 1 (1968).
[12] F. Ladieu and M. Sanquer, Ann. Phys. (Paris) **21**, 267 (1996); T. G. Castner, in *Hopping Transport in Solids*, edited by M. Pollak and B. Shklovskii (Elsevier Science, New York, 1991), p. 1.
[13] T. Fujiwara, S. Yamamoto, and G. Trambly de Laissardière, Phys. Rev. Lett. **71**, 4166 (1993).
[14] C. Sire, in *Lectures on Quasicrystals*, edited by F. Hippert and D. Gratias (Editions de Physique, Les Ulis-France, 1994), p. 505.
[15] J. X. Zhong, U. Grimme, R. A. Römer, and M. Schreiber, Phys. Rev. Lett. **80**, 3996 (1998).
[16] D. Mayou, in *Proceedings of the International Conference ICQ6* (Ref. [5]), p. 555.
[17] S. Roche and D. Mayou, Phys. Rev. Lett. **79**, 2518 (1997).
[18] C. Gignoux, Ph.D. thesis, Grenoble University, 1996 (unpublished).
[19] M. A. Chernikov, A. Bianchi, E. Felder, U. Gubler, and H. R. Ott, Europhys. Lett. **35**, 431 (1996).
[20] J. L. Gavilano, B. Ambrosini, P. Vonlanthen, M. A. Chernikov, and R. H. Ott, Phys. Rev. Lett. **79**, 3058 (1997).
[21] Z. Ovadyahu, J. Phys. C **19**, 5187 (1986).
[22] W. N. Shafarman, D. W. Koon, and T. G. Castner, Phys. Rev. B **40**, 1216 (1989).
[23] G. Grüner and A. Zawadowski, in *Progress in Low Temperature Physics*, edited by D. F. Brewer (North-Holland, Amsterdam, 1978), Vol. VIIB, p. 592.