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Evidence of the Relationship of the Electronic Properties of Icosahedral Boron-Rich Solids and Icosahedral Quasicrystals

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Optical conductivities and dielectric functions derived from the IR-optical reflectivity spectra exhibit clear similarities between icosahedral boron-rich structures and Al-based isosahedral quasicyrstals. This suggests a close qualitative relationship of their electronic structures. Accordingly icosahedral quasicrystals are assumed to be semiconductors with complex band structures qualitatively related to those of boron-rich solids, which are essentially determined by electron–phonon interactions. © 1997 Academic Press

INTRODUCTION

The large variety of boron-rich solids exhibits electronic properties, which are essentially determined by B_{12} icosahedra being the common structural elements of this group of materials. Though aluminum and gallium belong to the same group of elements in the periodic system and are therefore expected to generate at least approximately the same bonds, comparable crystal structures of elementary aluminum and gallium have not become known. However, together with other metal atoms these elements form icosahedral crystals and in particular icosahedral quasicrystals. Subsequently it will be shown that there are close similarities between specific electronic properties of the icosahedral boron-rich solids and Al-based icosahedral quasicrystals.

The electronic orbitals of the B_{12} icosahedra, which are slightly distorted in consequence of a Jahn–Teller effect, are split. This leads to a separation of unoccupied and occupied levels and accordingly the reason for the semiconductor character of the boron-rich solids, which has been unique for condensed systems of atoms with add electron numbers. The influence of the specific characteristics of the individual structures is obviously of secondary order only (1–3).

The electronic properties of the quasicrystals are not yet well understood. In most interpretations they were assumed to be metals because of the metal character of the ingredient atoms. Basic elements of the theoretical models concerned are a pseudogap (see, e.g., (4)) and a stability of the icosahedral phase due to an effective energy band factor according to the Hume–Rothery rule (see, e.g., (5, 6)).

However, recent experimental results demonstrate the electronic properties of the icosahedral quasicrystals to be untypical for intermetallic compounds. Degiorgi *et al.* (7) have shown that only a small portion of the charge carriers behaves as free electrons. Kimura *et al.* (8) were the first to show that the electrical conductivity is much lower than expected for metallic compounds, a result meanwhile confirmed by Klein *et al.* (9). Corresponding results were obtained by Biggs *et al.* on Al–Cu–Ru icosahedral crystals (10). Results of Pierce *et al.* (11) on Al–Pd–Re and of Tamura *et al.* (12) on highly ordered Al–Cu–Ru quasicrystals show that the transport characteristics are qualitatively similar to those of semiconductors. Optical results presented by Basov *et al.* (13) proved that $Al_{70}Pd_{20}Re_{10}$ is a semiconductor.

We assume that as in the boron-rich solids the icosahedral structure of such quasicrystals is responsible for their electronic properties (14) and prove this assumption by comparing characteristic spectra of optical conductivities and dielectric functions.

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SAMPLES AND THEIR PREPARATION

$Al_{92-X}Pd_XRe_8$-type quasicrystals with only slightly differing compositions ($X = 21$ and 20) were prepared by arc melting aluminum (99.99%), palladium (99.99%), and rhenium (99.99%) under Ar atmosphere. Each specimen obtained was remelted four to six times to ensure complete mixing. Then the samples were annealed for 48 hours at 1173 K to obtain a single quasicrystalline phase (for details see (12)).

As examples for the boron-rich solids, β-rhombohedral boron interstitially doped with V and Fe atoms and $ErAlB_{14}$ are considered (for the FIR dielectric functions of other boron-rich solids see Ref. (15)). The β-rhombohedral boron solid solutions were prepared by arc melting high-purity boron (Wacker 99.995%) and specpure metals and subsequently annealing the compounds for 30 hours at 1200 K to guarantee homogeneity (for details see (16)). $ErAlB_{14}$ was prepared by arc melting freshly ground crystalline boron (H. C. Starck, Goslar, FRG, 99.63% B, 0.15% C, 0.08% Si), α-AlB_{12} (Cerac, Milwaukee, WI, less than 1% impurities), and ErB_6, prepared as a master alloy from erbium metal (Cerac, 99.9%) and boron (for details, see (9)).

EXPERIMENTAL RESULTS

IR reflectivity spectra were measured with a FTIR spectrometer (Bruker IFS 113v) on high-grade polished surfaces; absorption spectra, optical conductivity, and dielectric functions were derived from the reflectivity spectra by Kramers–Kronig transformation. In principle, this requires that the spectra extend to a dispersion-free spectra range in particular toward high energies. To close this gap suitable extrapolations of the measured spectra were performed. Taking experimental results obtained at high photon energies (17, 18) into account, the interband transitions were simulated by suitable combinations of classical dispersion oscillators to that the presented ranges of the spectra are reliable within the accuracy of the measured reflectivity spectra.

Typical IR reflectivity spectra of VB_{32} for the boron-rich solids and $Al_{72}Pd_{21}Re_8$ for the icosahedral quasicrystals are shown in Fig. 1. Both exhibit a reflectivity strongly increasing toward low frequencies, which in the case of the boron-rich solids is proved to be caused by the dynamical conductivity (15). A corresponding interpretation of the spectra of quasicrystals seems possible.

In Figs. 2a and 2b the spectra of the optical conductivities of some boron-rich structures are compared with the corresponding spectra of the $Al_{71}Pd_{21}Re_8$ and $Al_{72}Pd_{20}Re_8$ quasicrystals measured with the same equipment, and additionally with the spectra of $Al_{63.5}Cu_{24.5}Fe_{12}$ (19), $Al_{70}Mn_9Pd_{21}$ (6), and $Al_{70}Pd_{20}Re_{10}$ (12) reproduced from the literature. The qualitative similarity of the spectra of both types of solids is obvious.

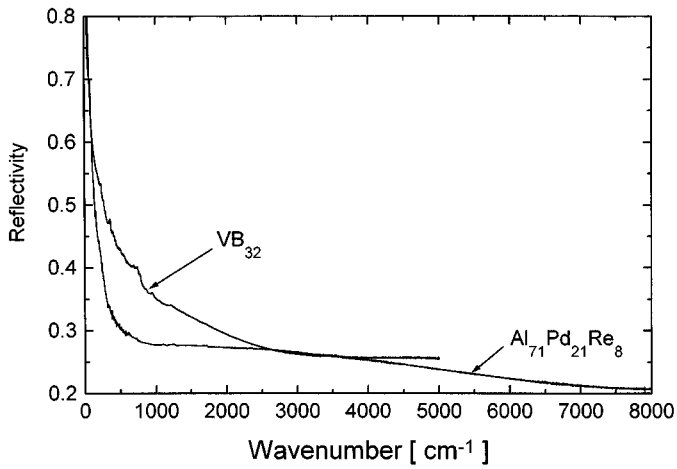

FIG. 1. Reflectivity spectra of the icosahedral boron-rich crystal VB_{32} and the icosahedral quasicrystal $Al_{71}Pd_{21}Re_8$.

Figures 3a and 3b show real and imaginary parts of the dielectric function of VB_{32} and $Al_{71}Pd_{21}Re_8$ respectively for wave numbers $\leq 200\ cm^{-1}$. In both cases the experimental

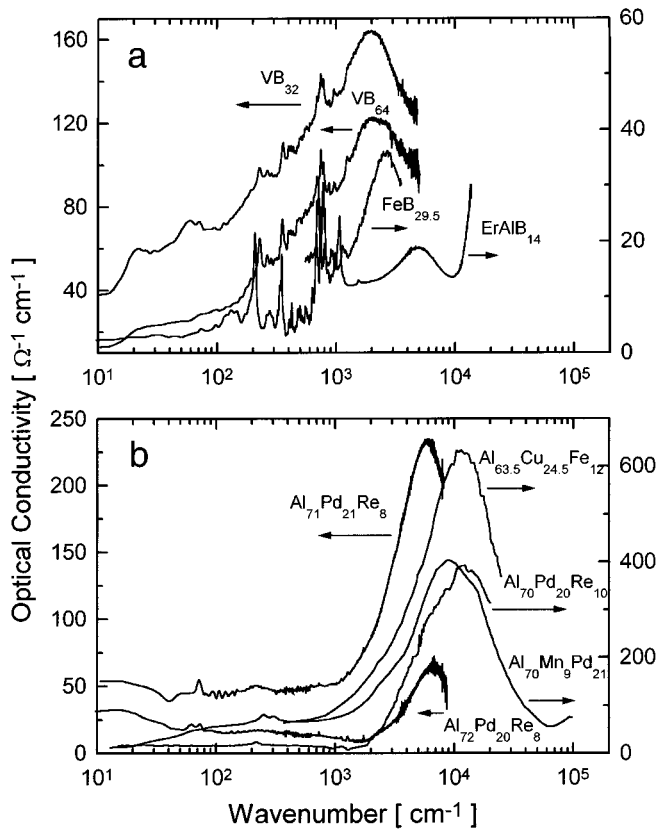

FIG. 2. Optical conductivities. (a) Highly doped solid solutions of β-rhombohedral boron with interstitially accomodated transition metal atoms and of the orthorhombic boride $ErAlB_{14}$. (b) Icosahedral quasicrystals $Al_{71}Pd_{21}Re_8$ and $Al_{72}Pd_{20}Re_8$. Spectra of $Al_{70}Pd_{20}Re_{10}$ (11) $Al_{63.5}Cu_{24.5}Fe_{12}$ (21), and $Al_{70}Mn_9Pd_{21}$ (7) reproduced from literature for comparison.

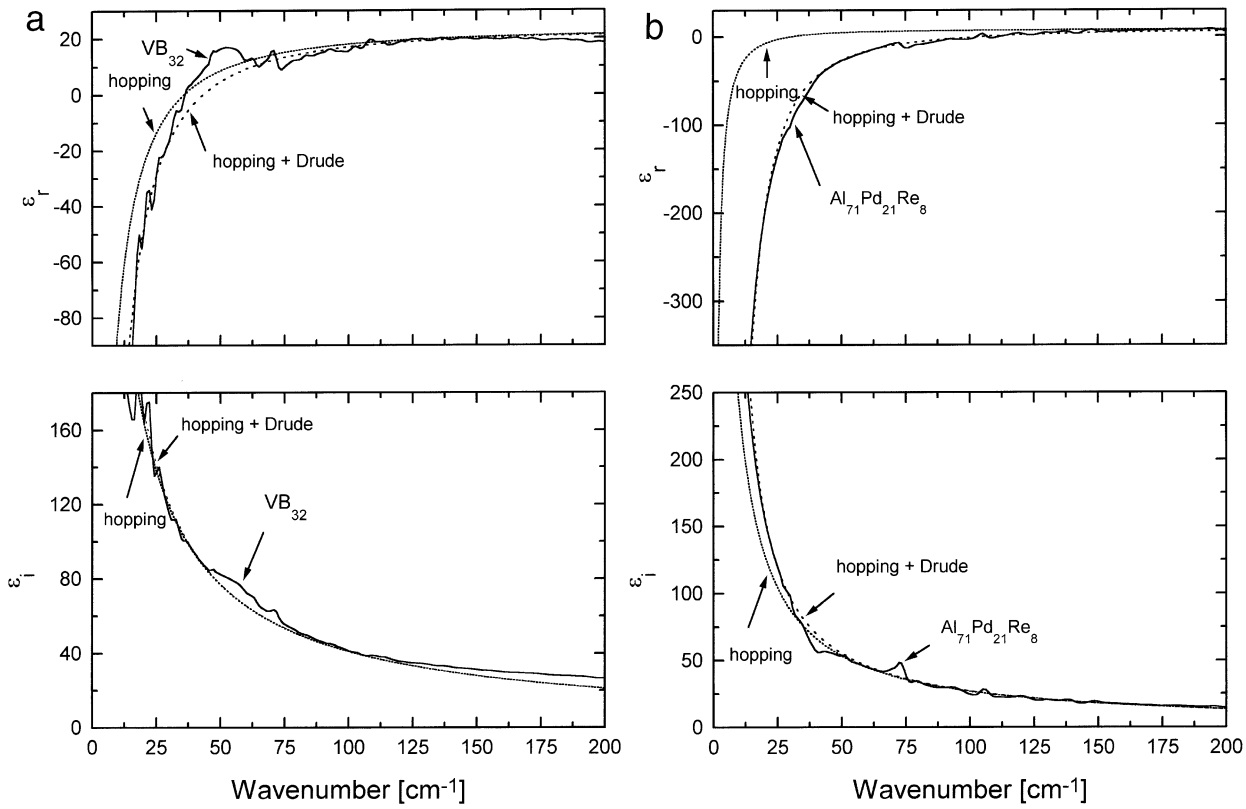

FIG. 3. Real and imaginary parts of the dielectric function vs wave number. Experimental results derived from the reflectivity spectra compared with model calculations based on hopping (after Butcher and Morys (20)) alone and on hopping and Drude-type plasma resonance both. (a) VB_{32}, (b) $Al_{71}Pd_{21}Re_8$.

curves could be satisfactorily fitted only when a superposition of classical Drude-type conductivity and of hopping processes is taken into account. To describe hopping at high frequencies the theory of Butcher and Morys (20) was used (for details see Refs. (14, 15)). The parameters used for fitting are listed in Table 1.

DISCUSSION

While the spectral positions of the optical conductivity maxima of the quasicrystals with Al_{12} icosahedra are roughly the same for different compositions, the intensity of the peaks varies considerably. Comparing at first our Al–Pd–Re compounds, whose compositions differ only by the exchange of 1 at.% Al by Pd, the strong dependence on the actual composition is obvious. This is underlined by the spectrum of $Al_{70}Pd_{20}Re_{10}$ (12), whose optical conductivity maximum is higher even by the factor 15. This strong dependence of electronic properties of Al–Pd–Re icosahedral quasicrystals on minor variations of the chemical composition is in accordance with the variation of the dc conductivities of numerous Al–Pd–Re quasicrystals measured by Honda *et al.* (21).

In general the optical conductivity maximum of the icosahedral quasicrystals are much higher than those of the β-rhombohedral boron structures, while the plasma edges

TABLE 1
Parameters of the Model Calculations to Fit the Measured Dielectric Functions in Figs. 3a and b

	Drude contribution			Hopping	
	ω_p (cm^{-1})	ω_τ (cm^{-1})	ε_h	a ($\Omega^{-1}\,cm^{-1}$)	ω_{ph} (cm^{-1})
β-rhombohedral boron structures					
VB_{32}	100	5.83	23	3.0	500
VB_{64}	50	5.31	23	1.1	500
$FeB_{29.5}$	—	—	9.5	0.09	500
Quasicrystals					
$Al_{71}Pd_{21}Re_8$	280	3.0	8.0	1.9	100
$Al_{72}Pd_{20}Re_8$	158	29.8	5.0	0.75	100

Note. Drude contribution: ω_p, plasma frequency; ω_τ, scattering frequency, ε_h, high frequency dielectric constant containing the contributions of bonded electrons and phonons. Hopping contribution: a, normalizing constant; ω_{ph}, phonon frequency (relevant for the hopping processes, rather insensitive parameter).

(Figs. 3a and 3b) are at similar spectral position. Irrespective of probably different effective electron masses, one reason seems to be that the ionization energies of the gap states in β-rhombohedral boron are obviously smaller than those in the icosahedral quasicrystals. This combination of higher ionization energies and higher densities of states is one reason that the plasma frequencies are similar to those of the boron structures. Indeed, for a final interpretation the quantitative density distribution of occupied states and the effective masses of the carriers are needed.

It is noteworthy that a 5% exchange of the Pd content by Al causes an increase of the peak absorption in the strong band of about 330%, and according to $\omega_p = \sqrt{4\pi Ne^2/m^* \cdot \varepsilon}$, a 20% change of the free electron concentration. Taking into account that the thermal excitation is essentially determined by the levels of lowest ionization energies, the different data seem consistent with the tail of the absorption band shifting to lower energies with increasing integral absorption.

CONCLUSION

The obvious similarity of characteristic optical properties of icosahedral boron-rich structures and Al-based icosahedral quasicrystals suggests a close qualitative relationship of their electronic structures, even though the different kinds of atoms and different arrangements of structural elements may of course lead to quantitative differences of band structure and transport parameters. Accordingly we assume icosahedral quasicrystals to be semiconductors with complex band structures, which are essentially determined by electron–phonon interactions as in icosahedral boron-rich structures. This conclusion is consistent with the results of dc measurements of icosahedral quasicrystals (8–12).

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