JOURNAL OF SOLID STATE CHEMISTRY 50, 304–311 (1983)

Preparation, Structure, and Properties of New Ternary Rhenium Arsenides and Phosphides with Metal–Metal Bondings

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Received April 26, 1983; in revised form July 18, 1983

The $M_2Re_5As_{12}$ arsenides (M = Fe, Co, Ni) and the $Co_2Re_5P_{12}$ phosphide were synthesized. The unit cell is orthorhombic with space group *Pnnm* and contains two formula units. The X-ray structure of $Ni_2Re_5As_{12}$ was studied from three-dimensional single-crystal counter data and was refined down to R = 0.048 for 637 independent reflections. The structure can be described as built up from two different structural domains; the first one is the marcasite type and shows As–As pairs and linear Re–Re chains, the second one consists of Re_4 clusters with common edges linked to terminal Ni atoms. A nearly temperature-independent paramagnetism and *p*-type metallic conduction were observed from the magnetic and electrical measurements. Also observed in this new family of compounds were the resistivities along and perpendicular to the **c** axis and their anisotropic behavior.

Introduction

Our previous results on ternary arsenides and phosphides containing both molybdenum or tungsten and a 3*d*-transition element dealt with structures involving nickel as the 3*d* element; indeed, their structures show linear and regular Mo–Ni–Mo (or W–Ni–W) chains, either of limited or of indefinite size (*1*, *2*).

More recently, we reported the existence of the first isolated metallic cluster in the chemistry of rhenium phosphides. This cluster involved the binary Re_6P_{13} form and was built up from four Re atoms in a planar distribution: two Re_3 triangles with one common edge (*3*).

It seemed to us of interest to prepare new ternary arsenides and phosphides comprising both nickel and rhenium in a metal : nonmetal ratio close to that found in Re_6P_{13}. In this manner, their structures would be expected to exhibit mixed Ni–Re bondings, either as chains or as clusters.

For the first time, we have succeeded in preparing one arsenide $Ni_2Re_5As_{12}$, the structure of which is partially derived from the marcasite type and shows effectively two kinds of metal–metal bonding along the **c** axis: Re_4 clusters with common edges linked to terminal Ni atoms, and linear infinite Re–Re chains. In the second attempt, two other arsenides, $Fe_2Re_5As_{12}$ and $Co_2Re_5As_{12}$, and one phosphide, $Co_2Re_5P_{12}$,

0022-4596/83 $3.00

were obtained and found to be isostructural with $Ni_2Re_5As_{12}$.

In this paper we present the synthesis and the structural results, as well as the physical properties, of this family of ternary compounds.

Experimental

1. Preparation

The compounds were prepared by direct combination of the elements in sealed evacuated silica tubes. The pure elements used as starting materials were powders of Fe, Co, Ni, Re (>99.9%), amorphous β arsenic (>99.999%), and red phosphorus (>99.99%).

The stoichiometric amounts of the elements, pressed into pellets, were annealed at 1000°C for several days after an initial treatment at 700°C to prevent a possible attack on the silica tubes by the rhenium. The synthesis of homogeneous samples required several intermediate grindings and annealings at 1000°C.

The preparation of the single crystals of the ternary arsenides was accomplished by the chemical vapor transport method using traces of iodine as transport agent. The transport tubes were 20 cm in length and 18 mm in outer diameter. The charge was maintained at 800°C and the growth zone was kept at 780°C. The transport process was maintained for 3 weeks; then the tubes were annealed for an additional 2 days at the growth-zone temperature. Needle-shaped single crystals obtained by this procedure measured up to 6 mm in length (Fig. 1). Attempts to prepare single crystals of the only $Co_2Re_5P_{12}$ phosphide using tin as flux were unsuccessful, leading always to mixtures of binary phosphides.

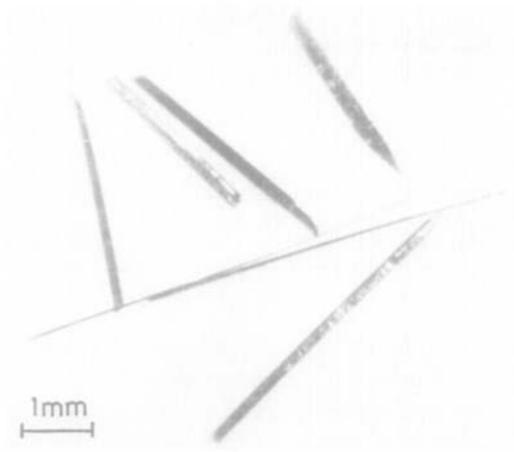

FIG. 1. Single crystals of the $Ni_2Re_5As_{12}$ phase.

2. X-ray Investigation

The phase analysis, carried out by X-ray powder methods, using a proportional counter diffractometer with Cu$K\alpha$ radiation, showed that the three arsenides $M_2Re_5As_{12}$ (M = Fe, Co, Ni) and the phosphide $Co_2Re_5P_{12}$ were isostructural. On the other hand, the X-ray patterns of the compositions "$Ni_2Re_5P_{12}$" and "$Fe_2Re_5P_{12}$" indicate mixtures in which the substituted MnP-type $Ni_{1-x}Re_xP$ and $Fe_{1-x}Re_xP$ phases were predominant ($0.5 \leq x \leq 0.75$).

The single-crystal investigation of $Ni_2Re_5As_{12}$, performed with the Weissenberg, Laue, and Buerger methods (Mo$K\alpha$ radiation), led to the following type of crystal lattice: orthorhombic unit cell, Laue symmetry *mmm*, possible space group *Pnn*2 or *Pnnm*, in agreement with the systematic absences of $0kl$: $k + l = 2n + 1$, $h0l$: $h + l = 2n + 1$ reflections. The lattice constants, obtained by using silicon (a = 5.43054 Å) as internal standard, volumes and density measurements (two formula units) are listed in Table I. The X-ray patterns of $Ni_2Re_5As_{12}$ and $Co_2Re_5P_{12}$ are shown in Fig. 2.

Structural Study of $Ni_2Re_5As_{12}$

1. Determination and Refinement

Intensity data of $Ni_2Re_5As_{12}$ were measured on an automatic four-circle Nonius

TABLE I

CELL DIMENSIONS, CALCULATED AND OBSERVED DENSITIES OF $Ni_2Re_5As_2$-TYPE COMPOUNDS

	a(Å)	b(Å)	c(Å)	V(Å^3)	d_{calc}	d_{obs}
$Ni_2Re_5As_{12}$	15.511(5)	12.432(4)	3.251(3)	627	10.32	10.16
$Co_2Re_5As_{12}$	15.593(5)	12.613(4)	3.251(3)	639	10.12	10.01
$Fe_2Re_5As_{12}$	15.632(5)	12.723(4)	3.282(3)	653	9.88	9.69
$Co_2Re_5P_{12}$	14.602(5)	11.973(4)	3.261(3)	570	8.27	8.14

TABLE II

CRYSTAL DATA FOR THE $Ni_2Re_5As_{12}$ SINGLE CRYSTAL

Single crystal dimensions (mm)	0.186 × 0.029 × 0.011
Linear absorption coefficient	μ = 762 cm^{-1}
Measurement conditions	h: 0–21 k: 0–17 l: 0–4
Measurement limits	$\theta < 30°$
Number of measured reflections	920
Number of independent reflections	671
Number of reflections used in refinement	641
Final value of R	0.048
Final value of R_ω	0.047

diffractometer with Zr-filtered Mo radiation. Conditions for the intensity measurements and dimensions of the single crystal are listed in Table II. An absorption correction was made using a program based on the indexes of the faces of the crystal (*4*). Lateral faces of the parallelepiped-shaped crystal were indexed according to the (120), ($\bar{1}$20), (1$\bar{2}$0), and ($\bar{1}\bar{2}$0) planes, the extreme faces, according to the (001) and (00$\bar{1}$) planes. The transmission factor was found to vary between 0.19 and 0.49, with an average value of 0.36.

The structure was solved in the *Pnnm* centrosymetric space group. The positions of the rhenium atoms were deduced from a three-dimensional Patterson function and the light atoms were located by difference Fourier synthesis. The structure was refined with a full-matrix least-squares program (*5*). The reliability factors R and R_ω,

$$R = \Sigma(||F_0| - K|F_c||)/\Sigma|F_0|$$

$$R_\omega = [\Sigma\omega(||F_0| - K|F_c||)^2/\Sigma\omega|F_0|^2]^{1/2},$$

where K is the scale factor and ω is the weight based on counting statistics (*6*),

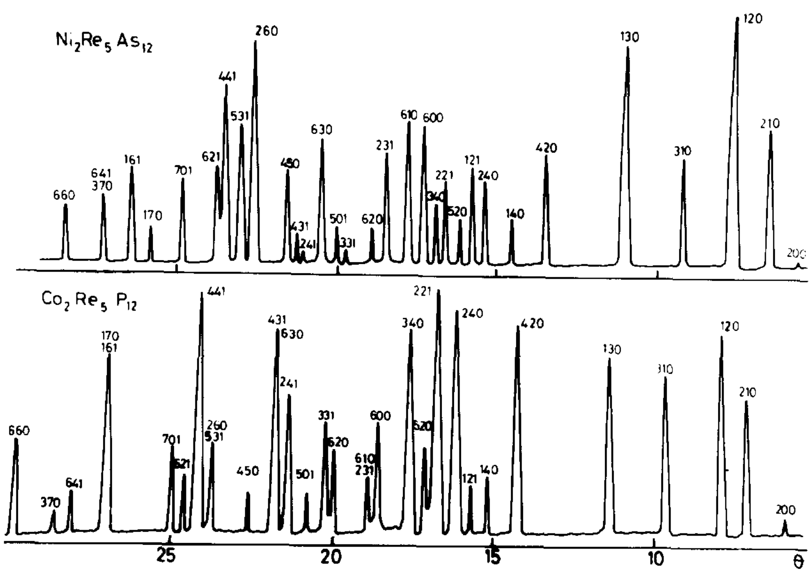

FIG. 2. X-ray patterns of $Ni_2Re_5As_{12}$ and $Co_2Re_5P_{12}$ (λCu$K\alpha$).

TABLE III

ATOMIC AND THERMAL COORDINATES OF $Ni_2Re_5As_{12}$

Atoms	Position	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	B_{eq} (Å^2)
Re_I	4g	0.3962(1)	0.8167(1)	0	3(1)	7(1)	871(24)	−1(1)	1.49
Re_{II}	4g	0.2388(1)	0.4207(2)	0	4(1)	7(1)	1187(28)	−1(1)	1.98
Ni	4g	0.1523(3)	0.6300(4)	0	5(2)	21(4)	339(54)	−3(2)	1.06
As_I	4g	0.4039(2)	0.4075(3)	0	2(1)	12(3)	205(41)	2(1)	0.61
As_{II}	4g	0.2381(2)	0.0678(4)	0	7(2)	38(4)	125(39)	−4(3)	1.19
As_{III}	4g	0.7582(2)	0.2222(4)	0	13(2)	45(5)	332(46)	−8(4)	1.80
As_{IV}	4g	0.0941(2)	0.1592(3)	0	7(2)	23(4)	181(41)	3(3)	0.95
As_V	4g	0.0769(2)	0.4643(3)	0	4(2)	25(4)	211(45)	2(2)	0.94
As_{VI}	4g	0.4413(2)	0.2081(3)	0	3(2)	12(3)	266(40)	−2(2)	0.73
Re_{III}	2a	0	0	0	5(1)	14(2)	278(29)	−4(2)	0.83

Note. The thermal factor is given by $\exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}$. The values of β are multiplied by a factor of 10^4. For all positions $\beta_{13} = \beta_{23} = 0$. The standard deviations are given in parentheses.

were, respectively, 0.048 and 0.047 after refinement of the positional and thermal parameters. A final difference-synthesis showed no peaks less than $-1\ e^-/\text{Å}^3$ or greater than $+1\ e^-/\text{Å}^3$. Attempts to refine the structure in the noncentrosymetric space group *Pnn*2 gave no proper results. The structure is thus described in space group *Pnnm*. The atomic and thermal coordinates are listed in Table III, the interatomic distances in Table IV.[1]

2. Description

A projection of the crystal structure on the (001) plane is shown in Fig. 3. The structure is characterized by three different rhenium and one nickel atoms which all occupy either distorted (Re_I, Re_{II}, Ni) or almost regular (Re_{III}) arsenic octahedra. Thus, the structure can be viewed as being built from these (MAs_6) octahedra (M = Re, Ni), coupled either by the faces ($NiAs_6$–$Re_{II}As_6$), the edges (Re_IAs_6–$Re_{II}As_6$), or the corners (Re_IAs_6–$Re_{III}As_6$, $Re_{II}As_6$–$Re_{III}As_6$) (Fig. 3).

The As atoms are surrounded by the metal atoms in three different ways. The As_I, As_{III}, As_{IV}, and As_{VI} atoms occupy tetrahedral sites: their neighbors are 3 Re + 1 As(As_I, As_{IV}), 3 Re + 1 Ni (As_{III}), or 2 Ni + 1 Re + 1 As(As_{VI}), respectively. The As_{II} atom is surrounded by five atoms (2 Ni + 2 Re + 1 As) in a square-planar pyramid arrangement, while the As_V atom occupies an approximately trigonal bipyramid (3 Re + 1 Ni + 1 As).

The arsenic atoms, except As_{III}, occur in pairs in the structure, namely, As_I–As_{VI}, As_{II}–As_{IV}, As_V–As_V pairs. The distances which vary between 2.484 and 2.525 Å, are very similar to those in Mo_2As_3 (2.445 Å) (*7, 8*) and in the marcasite-type arsenides (2.447 Å for β-$NiAs_2$) (*9–11*).

The average Ni–As (2.395 Å) and Re–As (2.485 Å) distances are approximately in agreement with those observed in NiAs (2.43 Å), $NiMo_2As_3$ (2.40 Å) (*7*), and in Re_3As_7 (2.55 Å) (*12*).

[1] During this investigation, weak super-reflections were observed on rotating the crystal and the Weissenberg photographs. The resulting structure which seems to correspond to an orthorhombic unit cell with the parameters $A = a$, $B = b$, $C = 3c$, is a (super) structure of the structure described here. Since the intensities of the super-reflections appeared too weak, no attempt was made to refine the (super) structure. This result may explain the high values of the β_{33} anisotropic coefficients in Table III.

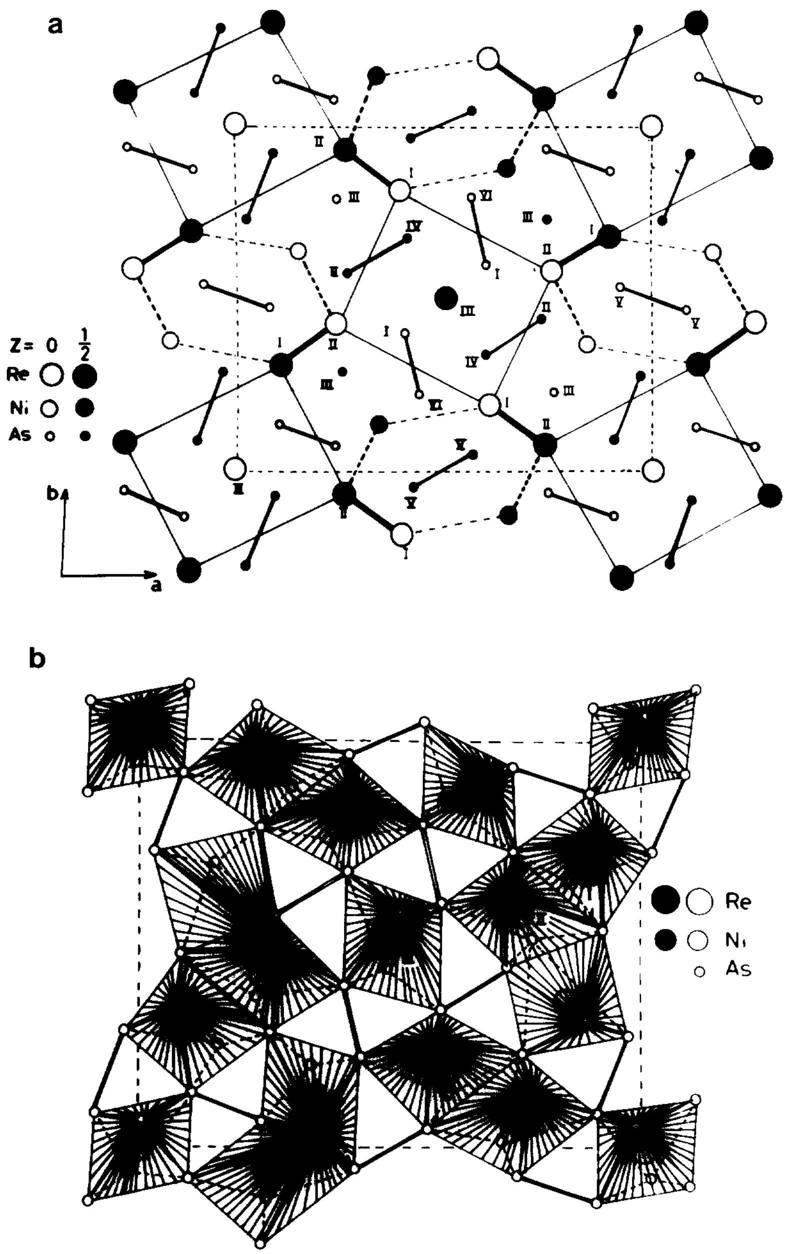

FIG. 3. Representation of the $Ni_2Re_5As_{12}$ structure. (a) Projection on the (001) plane. Broad dashed and full lines correspond to metal–metal and As–As bondings. The structural domains are indicated. (b) Disposition of the MAs_6 octahedra (M = Re, Ni). Double lines represent the As–As pairs.

3. Analogy and Structural Differences with the Marcasite Structure

The $Ni_2Re_5As_{12}$ structure shows two different structural domains. The first one is identical to the marcasite structure and can be observed at the origin and the center of the cell. In fact, the arrangement of the structure around the Re_{III} atoms corre-

TABLE IV

INTERATOMIC DISTANCES IN $Ni_2Re_5As_{12}$

Re_I–As_{III}	2.424(4)	Re_{II}–2 As_{III}	2.424(4)
–2 As_V	2.487(3)	–2 As_{II}	2.472(3)
–As_{VI}	2.519(4)	–As_I	2.549(3)
–2 As_{IV}	2.550(3)	–As_V	2.552(3)
–2 Re_{II}	2.944(2)	–Ni	2.903(2)
–2 Re_I	3.251(3)	–2 Re_I	2.944(2)
		–2 Re_{II}	3.251(3)
Re_{III}–2 As_{IV}	2.437(3)	Ni–As_{III}	2.280(2)
–4 As_I	2.487(3)	–As_V	2.354(3)
–2 Re_{III}	3.251(3)	–2 As_{VI}	2.393(4)
		–2 As_{II}	2.476(3)
		–Re_{II}	2.903(2)
		–2 Ni	3.251(3)
As_I–2 Re_{III}	2.487(3)	As_{II}–2 Re_{II}	2.472(3)
–As_{VI}	2.525(2)	–2 Ni	2.476(3)
–Re_{II}	2.549(3)	–As_{IV}	2.484(6)
–2 As_{III}	3.209(4)	–2 As_{III}	3.083(5)
–2 As_I	3.251(3)	–2 As_{II}	3.251(3)
As_{III}–Ni	2.280(2)	As_{IV}–Re_{III}	2.437(3)
–2 Re_{II}	2.424(4)	–As_{II}	2.484(6)
–Re_I	2.424(4)	–2 Re_I	2.550(3)
–2 As_{II}	3.083(4)	–2 As_{IV}	3.251(3)
–2 As_{III}	3.251(3)		
As_V–Ni	2.354(3)	As_{VI}–2 Ni	2.393(4)
–2 Re_I	2.487(3)	–Re_I	2.519(4)
–As_V	2.525(2)	–As_I	2.525(2)
–Re_{II}	2.552(3)	–2 As_{VI}	3.251(3)
–2 As_V	3.251(3)		

Note. Standard deviations in parentheses.

sponds exactly to that observed in the marcasite.

The marcasite structure (Fig. 4), which has the same space group as $Ni_2Re_5As_{12}$, is found for many transition-metal diarsenides and diphosphides (*13*) and shows metal atoms at the corner and the center of the orthorhombic unit cell, the nonmetal atoms being arranged in pairs. Half of these pairs are centered at the middle of the edges, and the other half at the middle of the faces. Each metal atom has a distorted octahedral coordination of six nearest nonmetal neighbors. Each nonmetal atom bonds to one nonmetal and three metal atoms in a distorted tetrahedral coordination. In most of the cases, no metal–metal bonding is encountered in the marcasite structure, the **c** axis of the unit cell being too large: for example, 3.544 Å in β-NiA_2, 3.840 Å in $NiSb_2$ (*11*).

Contrary to the marcasites where only one kind of metal or nonmetal atom exists, the Re_I and Re_{II} atoms of the $Ni_2Re_5As_{12}$ structure occupy the corners, while the Re_{III} atoms occupy the center of the marcasite arrangement (Fig. 3). In the same manner, there are two kinds of As–As pairs: As_I–As_{VI} and As_{II}–As_{IV} pairs. Finally, the small value of the **c** axis (3.251 Å) in the structure, 20% higher than the rhenium diameter (2.68 Å), leads us to regard the Re_{III}–Re_{III} interactions as producing linear and infinite Re–Re chains. The electrical measurements, reported below, also favor this interpretation. By analogy with the marcasite, this arrangement corresponds to the formula $ReAs_2$.

The second domain is quite different from the first one, being characterized essentially by metal–metal bonding. It can be found around the ($\frac{1}{2}0\frac{1}{2}$) and ($0\frac{1}{2}0$) positions in the unit cell. Three kinds of metal–metal bondings have to be considered which are derived from face-shared or edge-shared (MAs_6) octahedra (M = Re, Ni):

regular and zigzag Re_I–Re_{II} chains (dRe_I–Re_{II} = 2.944 Å);

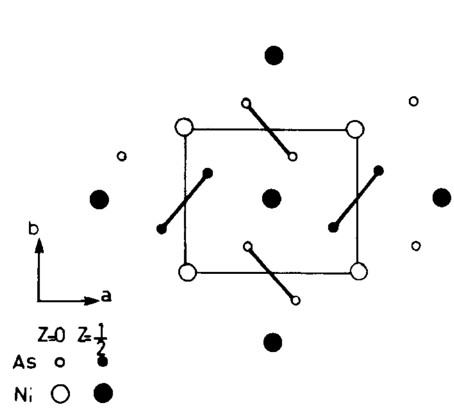

FIG. 4. Projection on the (001) plane of the β-$NiAs_2$ (marcasite-type) structure.

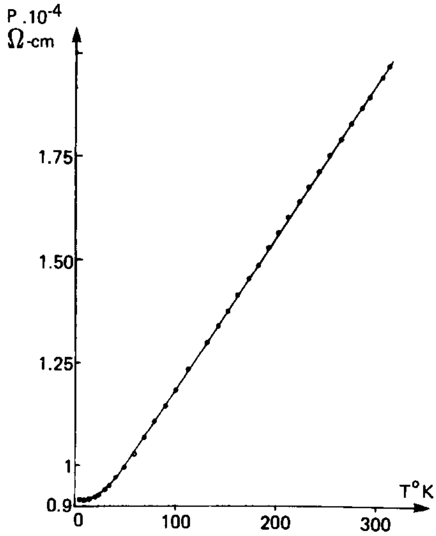

FIG. 5. Electrical resistivity $\rho_{\|}$ of $Ni_2Re_5As_{12}$ along the |001| direction.

$Ni{-}Re_{II}$ bondings ($dNi{-}Re_{II}$ = 2.903 Å) almost perpendicular to the chains ($Re_I{-}Re_{II}{-}Ni$ = 93°68);

$Re_I{-}Re_I$ and $Re_{II}{-}Re_{II}$ bondings along the **c** axis.

All these metal–metal bondings may be simply described as Re_4 clusters having common edges and linked to terminal Ni atoms. These clusters are stacked one above another in a ribbonlike manner which develops along the |001| direction (Fig. 6). The disposition in front of each other of two of these ribbons with their terminal Ni atoms close to the ($\frac{1}{2}0\frac{1}{2}$) and ($0\frac{1}{2}0$) positions leads to a channel into which the $As_V{-}As_V$ pairs are inserted (Fig. 3).

In summary, the $Ni_2Re_5As_{12}$ structure appears as a combination of the two structural arrangements described above. On one hand, two closely related marcasite-type or ribbonlike arrangements are separated from each other by As_{III} atoms, the only atoms not occurring as As–As pairs in the structure. On the other hand, two different arrangements are bound together by the Re_I or Re_{II} atoms.

Physical Properties

Magnetic measurements were performed using a Faraday method. The magnetic susceptibilities were measured in the temperature range 86 to 290 K, at a field strength of 5 kOe; all four compounds exhibit a nearly temperature-independent paramagnetism.

The susceptibilities of $Ni_2Re_5As_{12}$, before correcting for the core diamagnetism, are 0.65×10^{-6} and 0.59×10^{-6} emu/g at 86 and 290 K, respectively.

Electrical measurements were studied on needles of the $Ni_2Re_5As_{12}$ phase having a length of about 1 mm and a cross-section of $(2.5 \times 10^{-3}) \times (5 \times 10^{-3})$ cm^2. The longitudinal resistivity $\rho_{\|}$ along the **c** axis of the single crystal (direction of the Re–Re bonds) was measured by the four-point method using silver-painted contacts between 4 and 293 K, with a dc current or an ac low frequency bridge. The results given in Fig. 5 exhibit metallic behavior for this compound; the $\rho_{\|}$ values vary between 0.93×10^{-4} and 1.83×10^{-4} Ωcm at 4 and 293 K, respectively.

To evaluate the anisotropy, a resistivity measurement at room temperature was made on the same sample in a direction perpendicular to the Re–Re bonds. This transverse $\rho_{\perp}$ resistivity was performed by a two-probe method, the sample being held between two conductive plates. The contact resistance was measured separately. The deduced $\rho_{\perp}$ value was approximately 36×10^{-3} Ωcm.

A comparison between the $\rho_{\perp}$ and $\rho_{\|}$ values leads to a conductivity about 200 times higher along the Re–Re bonding direction. This conductivity is of *p* type, as observed from the thermoelectric power at room temperature.

Conclusion

The study of new ternary arsenides and a phosphide containing both rhenium and 3*d*-transition elements (Fe, Co, Ni) with a me-

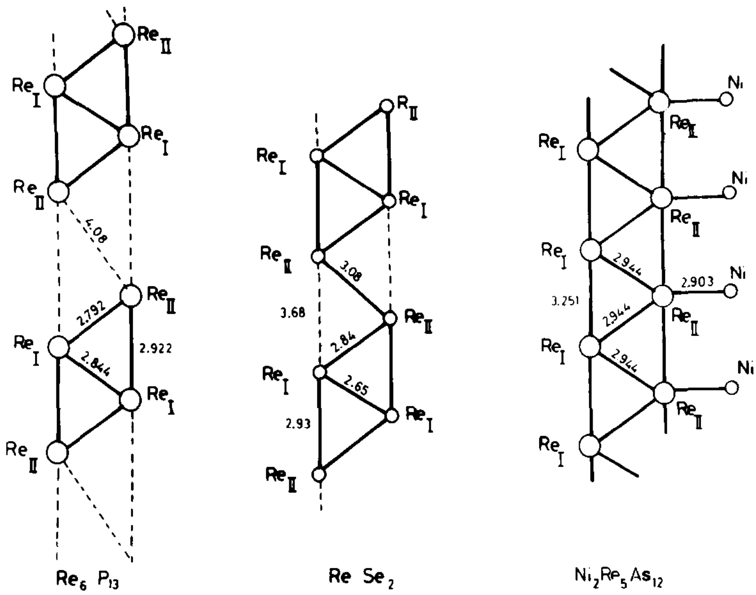

FIG. 6. Representation of Re_4 clusters in Re_6P_{13}, $ReSe_2$, and $Ni_2Re_5As_{12}$ structures. For this last structure, the Ni–Re bonding is almost perpendicular to the rhenium clusters.

tal : nonmetal ratio close to 0.5, exhibits a new structural type, in which Re_4 clusters linked to terminal Ni atoms are stacked one above another by sharing edges. This result may be compared with the structures of the binaries Re_6P_{13} or $ReSe_2$ (*3, 14*) (Fig. 6). In the first one, the Re_4 clusters are isolated from each other, being separated by large distances (4.08 Å); in the second one, these Re_4 clusters are linked together by Re_{II}–Re_{II} bondings (3.08 Å). The $Ni_2Re_5As_{12}$ structure corresponds to a new type of condensation of Re_4 clusters.

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