

Crystal Structure and Electrical Conductivity of Palladium Sulfide Bronzes MPd_3S_4 ($M = La, Nd, \text{ and } Eu$)

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Palladium sulfide bronzes MPd_3S_4 ($M = La, Nd, \text{ and } Eu$) were prepared in single phase. The bronzes are cubic with two M atoms in $(0, 0, 0; 1/2, 1/2, 1/2)$ and six palladium atoms in $(1/4, 0, 1/2\bar{2})$ positions. The sulfur positions $(x, x, x\bar{2})$ were determined with a guide of the R factors. The x values were $1/4$ for La and Nd compounds (i.e., space group $Pm\bar{3}n$), while a plot of the R factors of $EuPd_3S_4$ gave a very broad curve showing the x value rather displaced from $1/4$. This result is considered to be associated with the mixed valency of europium (Eu^{2+} and Eu^{3+}) in this compound. MPd_3S_4 ($M = La, Nd, \text{ and } Eu$) exhibited metallic conduction with the electrical conductivities decreasing with increasing temperature in the experimental range from ~ 15 K to room temperature. At 300 K, σ were 2.77, 2.42, and 2.28 Sm^{-1} for MPd_3S_4 ($M = La, Nd, \text{ and } Eu$), respectively. From the Hall coefficient measurements, the carriers were found to be the electrons with their numbers 1.71, 1.68, and 0.82 per unit cell of the crystals of $M = La, Nd, \text{ and } Eu$ compounds, respectively. These values suggest the formulas to be $M^{3+}(Pd_3^{2+}e^-)S_4^{2-}$ for La and Nd compounds, and to be $Eu_{0.5}^{2+}Eu_{0.5}^{3+}(Pd_3^{2+}e_{0.5}^-)S_4^{2-}$ for Eu compound. © 1997 Academic Press

INTRODUCTION

There have been a number of studies on preparation and characterization of cubic platinum oxide bronzes $M_xPt_3O_4$ ($M = Li, Na, Ni, Cd, \text{ etc. and } 0 < x \leq 1$). Yet, no platinum sulfide bronzes of the type $M_xPt_3S_4$ seem to exist. Instead, the compounds having the same S/Pt atom ratio but two alkali metal atoms in the formula, i.e., $Rb_2Pt_3S_4$ and $Cs_2Pt_3S_4$, have been prepared (1). These compounds are of an orthorhombic system with a layer structure of the type similar to the corresponding palladium compound, monoclinic $Cs_2Pd_3S_4$ (2, 3), in which the S–Pd–S layers infinitely span two-dimensionally the planes normal to the b -axis. Also, the compounds $K_2Pd_3S_4$ and $Rb_2Pd_3S_4$ with a stacking variation of the layer structure of $Cs_2Pd_3S_4$ have been prepared (4). They consist of four layers per unit cell. These compounds not only contain two alkali metal atoms in the formula, but crystallize in the structures largely differ-

ent from that of $M_xPt_3O_4$ on account of their layer structures.

Isotropic sulfide bronzes have been prepared only with palladium. Keszler and Ibers (5) have first synthesized $LaPd_3S_4$, $TbPd_3S_4$, and $SmPd_3S_4$ from a stoichiometric combination of the elements heated at 1125 K in a sealed evacuated quartz tube. The crystal was of the ideal $NaPt_3O_4$ type, with its magnetism basically being that derived from the trivalent $4f$ rare-earth ions as shown by the effective Bohr magneton numbers obtained by magnetic susceptibility measurements.

In their succeeding paper, Keszler *et al.* (6) synthesized more compounds of MPd_3S_4 type (i.e., $M = Y, La, Ce, Pr, Sm, Tb, Ho, \text{ and } Er$), for which refinement of the crystal structure was performed by X-ray and neutron diffraction analyses. They discussed the correlation of the lattice parameters of the cubic MPd_3S_4 with the crystal radii in relation with the bonding nature and the M –S, Pd–S, and S–S separations calculated on the assumption of ideal structure of $Pm\bar{3}n(O_h^3)$ for these sulfides.

Keszler *et al.* (6) also measured the magnetic susceptibilities of MPd_3S_4 ($M = Pr, Sm, Tb, \text{ and } Ho$) at temperatures from liquid He temperature to room temperature, in which the consistency with their earlier result was confirmed. Moreover, the electrical conductivity was measured for $LaPd_3S_4$ as a function of temperature between 100 and 300 K. The compound was metallic, exhibiting a decreasing conductivity with increasing temperature.

In a course of the studies on the palladium sulfide bronzes, MPd_3S_4 , a variety of compounds with different M atoms (rare-earth elements) have been prepared. However, the synthesis of $NdPd_3S_4$ has not been reported yet. In this work, we prepared $NdPd_3S_4$, $LaPd_3S_4$, and $EuPd_3S_4$ in single phase. $EuPd_3S_4$ has not been prepared in a single phase but as a mixture with other compounds (6). The sulfur position in these compounds was determined for the powder X-ray data using the Rietveld method. The electrical conductivity and Hall coefficient were measured in a temperature range between ~ 15 K and room temperature. We will follow with a discussion on their bonding and transport properties.

EXPERIMENTAL

1. Preparation of Rare-Earth Sulfides

Rare-earth sesquioxides (La_2O_3 , Nd_2O_3 , and Eu_2O_3) of 99.9% purity were obtained from Nihon Yttrium Co., Ltd. The sesquioxide was dissolved in 3 M H_2SO_4 by heating on a hot plate at around 373 K. The solution was evaporated to near dryness, and the rare-earth sulfate solid was transferred into a quartz boat. The boat was then placed in the uniform temperature zone of a clamshell tube furnace. The reaction system was evacuated, and then dry N_2 gas was introduced. Subsequently, H_2S gas was flowed through the reaction tube at a rate of 50 ml/min. The furnace temperature was raised to 1173 K and kept for 3 h, followed by cooling to room temperature. After the reaction system was replaced by N_2 , the product was taken out, and the phase and crystal structure analyses were made by powder X-ray diffraction. The obtained compounds were identified as La_2S_3 , Nd_2S_3 , and EuS .

2. Synthesis of MPd_3S_4 Ternary Sulfides

The calculated amount of the rare-earth sulfide, palladium powder of 99.9% purity obtained from Mitsuwa Chemicals Co. and sulfur of 99.999% purity obtained from Kanto Chemical Co., Inc. were finely mixed in an agate mortar. The mixture was put into a quartz tube, evacuated, and sealed. Then, the ampoule was heated at 1173 K for 3 d in a muffle furnace. After gradual cooling of the sample to room temperature, the product powder was subjected to powder X-ray analysis. For preparation of the sample for electrical conductivity measurements, the product was pelletized into a disk of 10 mm diameter and ~ 1 mm thickness by using a uniaxial press at 20 MPa. Then, the pellet was sintered at 1173 K for 4 h in a flow of 100 ml/min H_2S .

3. X-Ray Diffraction Analysis

X-ray diffractometry was carried out using a Rigaku RAD-IC diffractometer using $\text{CuK}\alpha_1$ ($\lambda = 1.54056 \text{ \AA}$) radiation (40 kV, 20 mA) monochromatized with curved pyrolytic graphite. The slit system was 1° – 1° – 0.15 – 0.3 mm. The intensity and least-squares lattice parameter calculations were carried out with the LAZY-PULVERIX (7) and LCR2 (8) programs, respectively. The program RIETAN (9) was used for refining the diffraction data by the Rietveld method.

4. Electrical Conductivity and Hall Coefficient Measurements

The electrical conductivity and Hall coefficient were measured by the four-probe van der Pauw method (10). At four diagonal points of the sintered pellet, the thin film of

gold was vapor-deposited. Fine copper wires were soldered on the film. After the pellet was set to the measuring device, it was cooled to ~ 15 K in a vacuum by a Daikin UV202CL helium refrigerator. Then, the temperature of the pellet was raised to room temperature with a tape-heater at a rate of 0.5 K/min by controlling the rate with a Chino KP-1000 digital programmer measuring the electrical conductivities every 1 min. By applying a constant current of 300 mA (Advantest TR-6143) to the sample, the potential drop was measured by a Keithley Model-182 voltmeter of which the input impedance was > 10 G Ω . The hysteresis in the electrical conductivity was checked by lowering the temperature at the same rate from room temperature to ~ 15 K.

Hall coefficients were measured at temperatures of 50, 100, 150, 200 K, and room temperature. The magnetic field of 0.58 T was applied perpendicular to the sample with a Tamagawa WVM-3 electromagnet. The effect of magnetoresistance was minimized by changing the directions of the field and current, followed by averaging the Hall voltages.

RESULTS AND DISCUSSION

In the upper part of Fig. 1, the observed data points of the powder X-ray diffraction intensities which were collected for 1.2 s with an 0.02° (2θ) step angle for NdPd_3S_4 are shown. The solid line depicts the calculated peaks as obtained by the Rietveld method (RIETAN program (9)) from these points. No observed peaks other than the ones corresponding to the simple cubic NaPt_3O_4 -type crystal structure (11) are seen. From the difference intensity pattern of the I_{obs} and the refined I_{calc} given in the lower part of the same figure, the agreement of the I_{obs} and I_{calc} is seen to be satisfactorily good. The same results were obtained for LaPd_3S_4 and EuPd_3S_4 .

The lattice parameters of cubic LaPd_3S_4 , NdPd_3S_4 , and EuPd_3S_4 were calculated by Nelson–Riley least-squares method on the LCR2 program to be 6.7369, 6.6864, and

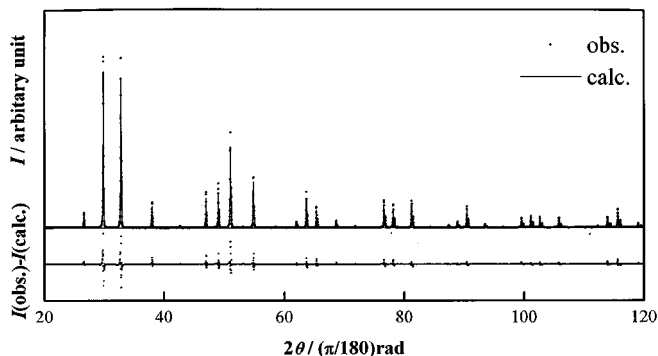


FIG. 1. Final Rietveld refinement and difference profile for NdPd_3S_4 .

6.6765 Å, respectively. The decrease of the lattice parameter with increasing atomic number of the rare-earths in the above compounds is thought to reflect the crystal radius contraction in these elements (12, 13).

As for the space group of the $M_xPt_3O_4$ and MPd_3S_4 compounds, two possibilities have been argued. If $Pm\bar{3}n(O_h^3)$, the atom positions are 2 M in $(0, 0, 0; 1/2, 1/2, 1/2)$, 6 Pt (or Pd) in $(1/4, 0, 1/2\bar{C})$, and 8 O (or S) in $(1/4, 1/4, 1/4\bar{C})$. On the other hand, if the space group is $P\bar{4}3n(T_d^4)$, while the atom positions for 2 M and 6 Pt (or Pd) are the same as those of $Pm\bar{3}n$, the positions for 8 O (or S) are changed to $(x, x, x\bar{C})$. Keszler *et al.* (6) assumed the structure of $LaPd_3S_4$ to be centrosymmetric $Pm\bar{3}n$ since the refinement with $x \neq 1/4$ afforded higher R values. In this work, the refinement of the structures of $LaPd_3S_4$, $NdPd_3S_4$, and $EuPd_3S_4$ was carried out by minimizing $R = \sum |I_{obs} - I_{calc}| / \sum I_{obs}$. The R values were calculated together with isotropic temperature factors on the RIETAN program using the atomic scattering factors for La, Nd, Eu, Pd, and S atoms obtained by Cromer and Waber (14). The anomalous dispersion corrections were made with the values of Cromer (15).

In Fig. 2, a plot of the R values for $LaPd_3S_4$ against the position parameter x is shown. The minimum of the R value of 5.3% was obtained at $x = 0.25$, in good agreement with the result of Keszler *et al.* for the same compound (6). Figure 3 is the same plot for $NdPd_3S_4$. This compound also gives the minimum R value of 4.7% at $x = 0.25$. These results are considered to suggest that the space group for $LaPd_3S_4$ and $NdPd_3S_4$ is $Pm\bar{3}n$.

The plot of the R values for $EuPd_3S_4$, however, shows a wide range of x values from $x = 0.24$ to 0.26, where the R values are all close to the lowest (Fig. 4). Possibly, the curve exhibits two shallow minima at $x = 0.25$ and 0.26, where the R values are $\sim 5.8\%$ which is a little higher than those of $LaPd_3S_4$ and $NdPd_3S_4$. The crystal structure or the sulfur positions of $EuPd_3S_4$ seem to be significantly different from those of $LaPd_3S_4$ and $NdPd_3S_4$. Similar behavior has been reported for $Ni_{0.25}Pt_3O_4$ having nickel nonstoichiometry. This compound gives two minima of the R value around $x = 0.22$ and 0.28 (16). Shannon *et al.* (17) observed that in $Li_{0.64}Pt_3O_4$ the oxygen atoms move away from the special position $(1/4, 1/4, 1/4\bar{C})$ lowering the space group symmetry from $Pm\bar{3}n$ to $P\bar{4}3n$. They also describe that such structural deformations could be associated with the metal deficiency in the compounds of this type. In the neutron diffraction study on sodium nonstoichiometric $Na_{0.73}Pt_3O_4$, peak widths 30–50% broader than $Na_{1.0}Pt_3O_4$ have been observed (18). It seems likely from these results that the distortion of the square planar coordination of oxygen around platinum is related to the random occupancy of nonstoichiometric M atoms in the crystal. The platinum ions cannot be completely stabilized in the square planar d^8 complex through dsp^2 hybridization since the

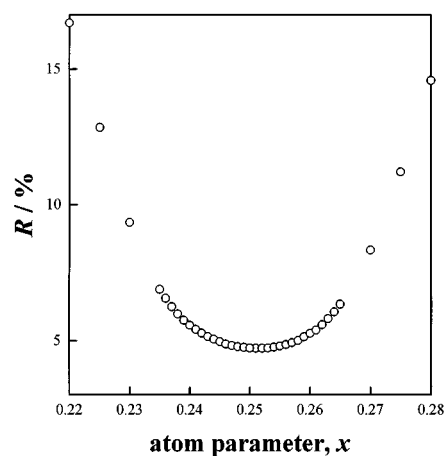


FIG. 2. R factor of $LaPd_3S_4$ as a function of atom parameter of sulfur.

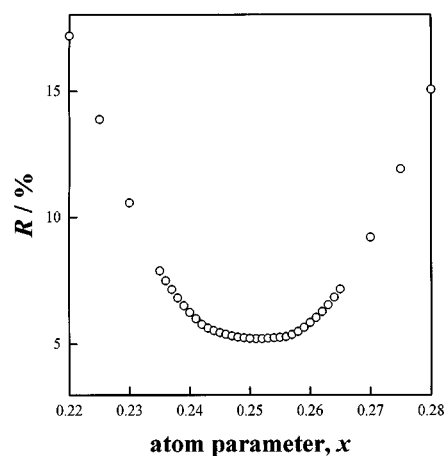


FIG. 3. R factor of $NdPd_3S_4$ as a function of atom parameter of sulfur.

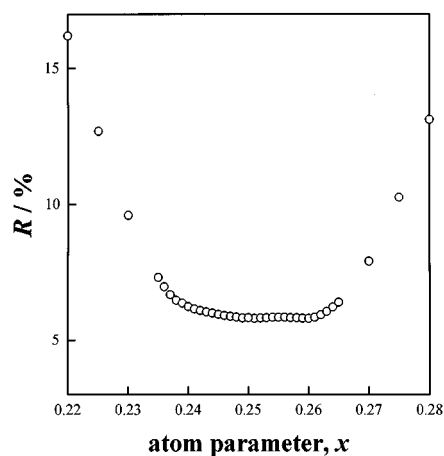


FIG. 4. R factor of $EuPd_3S_4$ as a function of atom parameter of sulfur.

electron number should be smaller than eight due to the deficiency of the M metal ions (19), which is assumed to cause the deformation of the oxygen coordination.

Efforts to effect the chemical analysis of composition of MPd_3S_4 ($M = La, Nd, \text{ and } Eu$) were unsuccessful because these compounds would not dissolve even in hot aqua-regia. But the increased concentration of random vacancy at sulfur (x, x, x) position for MPd_3S_4 ($M = La, Nd, \text{ and } Eu$) did not improve the R value. The introduction of vacancies, which are randomly distributed on the $2M$ ($0, 0, 0$; $1/2, 1/2, 1/2$) positions, also increased the R value: There may be no M metal and sulfur nonstoichiometries. Therefore, the existence of the two minima of the R value in the europium compound is considered to be caused not by nonstoichiometry but by the mixed valency of Eu^{2+} and Eu^{3+} . In $M^{3+}Pd_3S_4$, the formal valency of palladium is $+5/3$ (< 2). Since the electron configuration of palladium is $4d^{10}$, the mean electron number of this element ($10 - 5/3 = 8.3$) is larger than eight. This state might be stable for palladium sulfur bronze, and the admixture of Eu^{2+} lowers the stability of the compound leading to the deformation of the square planar coordination of sulfur atoms around a palladium atom. The reason of the decreased stability toward the palladium d^8 state for these compounds is not now clear. The unit cell of MPd_3S_4 crystal is illustrated in Fig. 5.

The crystal data for $LaPd_3S_4$, $NdPd_3S_4$, and $EuPd_3S_4$ after Rietveld refinements are given in Table 1, where the $EuPd_3S_4$ interatomic distances are those for space group $Pm\bar{3}n$. The isotropic temperature factors of the present compounds can be discussed in comparison with those of the other compounds with the same crystal structure. For $Ni_{0.25}Pt_3O_4$, the values $\beta_{11}(Pt) = 0.14$, $\beta_{22}(Pt) = 0.16$, $B(Ni) = 2.0 \text{ \AA}^2$ and $B(O) = 3.2 \text{ \AA}^2$ have been obtained (16). For $Cd_{0.3}Pt_3O_4$, the temperature factors are $B(Pt) = 0.6$,

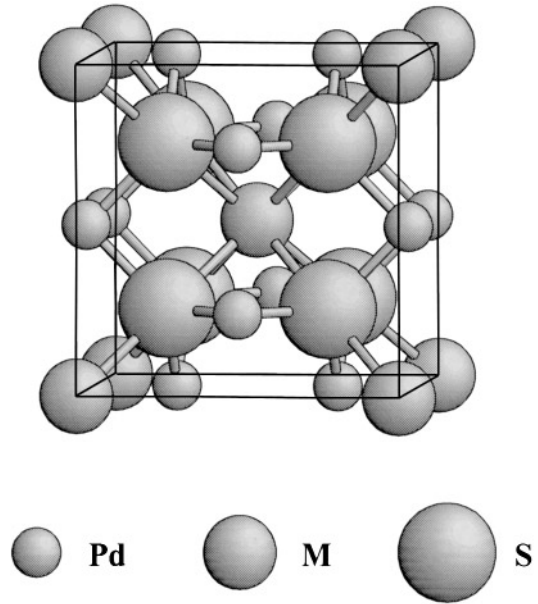


FIG. 5. Sketch of MPd_3S_4 ($M = La, Nd, \text{ and } Eu$) structure.

$B(Cd) = 2.5$, and $B(O) = 1.9 \text{ \AA}^2$ (20). On the other hand, for palladium sulfide bronze $U_xPd_3S_4$ ($0.9 < x < 1$), the values are $B(Pd) = 1.18$, $B(U) = 1.08$, and $B(S) = 1.05 \text{ \AA}^2$ (21). The temperature factors for $LaPd_3S_4$, $NdPd_3S_4$, and $EuPd_3S_4$ in this work are still smaller than those for $U_xPd_3S_4$.

The electrical conductivity of the three compounds was measured for the pellets with ca. 70% of theoretical density. The pellets for the measurements were prepared by pressing at 20 MPa in a die of 10 mm \varnothing and by succeeding sintering in H_2S at 1173 K. The variation of conductivity with temperature is illustrated in Fig. 6 for $LaPd_3S_4$, $NdPd_3S_4$, and $EuPd_3S_4$ specimens. Since no significant hysteresis loops

TABLE 1
Crystal Data after Refinements

	$LaPd_3S_4$	$NdPd_3S_4$	$EuPd_3S_4^a$
Lattice parameter $a/\text{\AA}$	6.7369 ± 0.0002	6.6864 ± 0.0004	6.6765 ± 0.0005
$B(M)/\text{\AA}^2$	0.47 ± 0.02	0.40 ± 0.02	0.43 ± 0.02
$B(Pd)/\text{\AA}^2$	0.56 ± 0.02	0.44 ± 0.02	0.21 ± 0.02
$B(S)/\text{\AA}^2$	0.48 ± 0.02	0.44 ± 0.02	0.47 ± 0.02
Interatomic distances/ \AA			
$d(M-S)$	2.9171 ± 0.0001	2.8953 ± 0.0002	2.8910 ± 0.0002
$d(Pd-S)$	2.3818 ± 0.0001	2.3640 ± 0.0001	2.3605 ± 0.0002
$d(M-M)$	5.8343 ± 0.0002	5.7906 ± 0.0003	5.7820 ± 0.0004
$d(Pd-Pd)$	3.3685 ± 0.0001	3.3432 ± 0.0002	3.3383 ± 0.0003
$d(M-Pd)$	3.7660 ± 0.0002	3.7378 ± 0.0002	3.7323 ± 0.0003
$d(S-S)$	3.3685 ± 0.0001	3.3432 ± 0.0002	3.3383 ± 0.0003
R factor/%	4.73	5.23	5.84

^a Interatomic distances are those for space group $Pm\bar{3}n$.

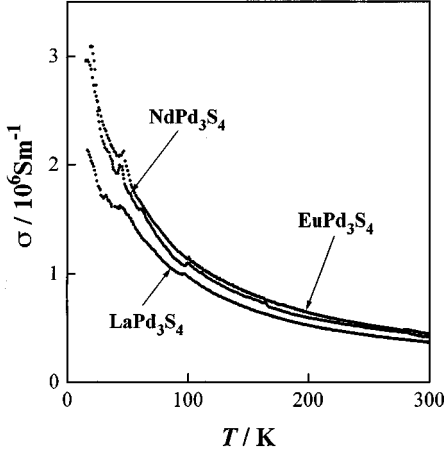


FIG. 6. Electrical conductivity of MPd_3S_4 ($M = \text{La, Nd, and Eu}$) as a function of temperature.

were observed for the conductivity values of these samples in the heating and cooling processes, the averaged values of the two processes are plotted in this figure. The electrical conductivity of LaPd_3S_4 at 300 K, $3.6 \times 10^5 \text{ Sm}^{-1}$, is about 6×10^{-3} of that of copper, since the conductivity of copper is $5.98 \times 10^7 \text{ Sm}^{-1}$ at 298 K (22). However, our value is about 10^3 of the electrical conductivity of LaPd_3S_4 at the same temperature, $4 \times 10^2 \text{ Sm}^{-1}$, measured by Keszler *et al.* (6). The reason for this discrepancy is not clear but it is possible that a small difference of stoichiometry in the compound could have caused the larger change of the electrical conductivity. Our samples for the electrical conductivity measurements were prepared by sintering the pelletized bronzes in H_2S at 1173 K for 4 h, while Keszler *et al.* treated the sample in a flow of CS_2 at 700 K for 2 h. Both results are, on the other hand, in agreement in the point that the conductivity decreases with increasing temperature below the room temperature. The high conductivities and the temperature dependence as seen for LaPd_3S_4 show that the conduction is metallic for this compound in line with Ref. (6). From Fig. 6, it is seen that NdPd_3S_4 and EuPd_3S_4 are also metallic.

Figure 6 shows that the conductivity curves for the three bronzes are not far apart. The conductivity is the highest for NdPd_3S_4 and the lowest for LaPd_3S_4 . The temperature dependence of specific resistivity is given in Fig. 7, which indicates that ρ increases almost linearly with increasing temperature in a range between $\sim 15 \text{ K}$ and room temperature. Such a linear increase is in accord with the theoretical prediction from the electron-phonon interaction that the slope is $8\pi^2 k_B \lambda \hbar^{-1} \omega_p^{-2}$ (23) or more simply $aM^{-1}\Theta_D^{-2}$ (24), where λ is the interaction parameter, ω_p is the plasma frequency, and a , M and Θ_D are the proportionality constant, the mass of the atoms and the Debye temperature, respectively. The slopes are obtained from Fig. 7 as

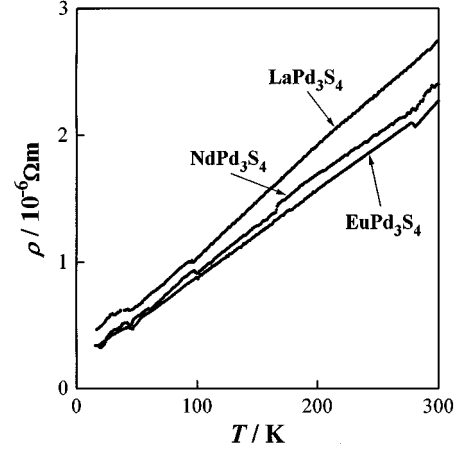


FIG. 7. Specific resistivity of MPd_3S_4 ($M = \text{La, Nd, and Eu}$) as a function of temperature.

$8.25 \times 10^{-9} \text{ } \Omega\text{mK}^{-1}$ for LaPd_3S_4 and $7.15 \times 10^{-9} \text{ } \Omega\text{mK}^{-1}$ for NdPd_3S_4 and EuPd_3S_4 . Therefore, assuming that the masses of the atoms are the same for the three compounds, a following relation will hold for the Debye temperatures, i.e., $\Theta_D(\text{NdPd}_3\text{S}_4) = \Theta_D(\text{EuPd}_3\text{S}_4) = 1.07\Theta_D(\text{LaPd}_3\text{S}_4)$.

The Hall coefficients measured at 50, 100, 150, 200 K, and room temperature are listed in Table 2. A marked fluctuation was observed in the Hall voltage with time during measurement. It was small at room temperature but was enhanced larger at lower temperatures. This fluctuation is assumed to be caused by some electric noises in the measuring apparatus or by polarization of the sample. According to Waser and McClanahan (25), a steady decrease of current was observed due to polarization for metallic NaPt_3O_4 immediately after application of a potential at 77 K, but this effect was less marked at room temperature. Although the R_H values in Table 2, each of which is the average of 10 measurements, still show a significant scattering, they do not seem to have any temperature dependence, i.e., the carrier concentration remains unchanged with temperature. From the polarity of the Hall voltage, the carriers were found to be electrons. In Table 3, the Hall coefficients, Hall mobilities, and carrier concentrations per unit cell at room temperature are given. If the rare-earth and sulfur ions have

TABLE 2
Hall Coefficients, $R_H/10^{-9} \text{ m}^3\text{C}^{-1}$, at Different Temperatures

T/K	LaPd_3S_4	NdPd_3S_4	EuPd_3S_4
50	-1.14	-0.95	-2.43
100	-1.22	-0.77	-2.61
150	-1.38	-0.86	-2.68
200	-1.37	-0.83	-2.73
Room temperature	-1.12	-1.11	-2.26

TABLE 3
Electrical Data at Room Temperature

	$\rho/10^{-6} \Omega\text{m}$	$R_H/10^{-9} \text{m}^3\text{C}^{-1}$	$\mu/10^{-4} \text{m}^2\text{V}^{-1}\text{s}^{-1}$	n_c^a
LaPd ₃ S ₄	2.67	-1.12	4.27	1.71
NdPd ₃ S ₄	2.35	-1.11	4.72	1.68
EuPd ₃ S ₄	2.26	-2.26	10.00	0.82

^a Number of carriers per unit cell.

+ 3 and - 2 formal valencies, respectively, there would be one electron per formula which is loosely trapped to the palladium atoms as $M^{3+}(\text{Pd}_3^{2+}e^-)\text{S}_4^{2-}$. Since the unit cell contains two formula units, the electron concentration becomes two per cell. The measured carrier concentrations for LaPd₃S₄ and NdPd₃S₄ shown in Table 3 are close to the predicted value of two, although about 15% smaller. On the other hand, the measured carrier concentration of 0.82 for EuPd₃S₄ is not consistent at first sight. However, if the half of the europium atoms in the compound are in a divalent state, the formula would be $\text{Eu}_{0.5}^{2+}\text{Eu}_{0.5}^{3+}(\text{pd}_3^{2+}e_{0.5}^-)\text{S}_4^{2-}$. The number of electrons per unit cell is one in this case, which is in agreement with the result of the Hall effect measurements also within ca. 15%. This 15% difference could be explained as the corresponding number of electrons are strongly coupled with the palladium atom and do not contribute to the electrical conduction.

The mixed valency of europium in EuPd₃S₄ was confirmed by Mössbauer spectrometry (26). The Mössbauer spectra of this compound at room temperature were composed of one single peak of Eu^{2+} and one single peak of Eu^{3+} . From the ratio of the peak areas, the concentration ratio of the ions was obtained to be $\text{Eu}^{2+}:\text{Eu}^{3+} = 47.3:52.7$. The Mössbauer data are in accord with the result of the Hall effect measurements.

The metallic conduction in metallic oxides is supposed to take place through either direct metal-metal interactions forming a narrow, cation-sublattice *d* band or metal-oxygen-metal interactions to form a wide π^* band (27). Cahen *et al.* (28) conceived that the conduction of electrons in platinum (oxide) bronze is possibly based on the direct metal-metal interactions since the Pt-Pt distance in these bronzes is short (2.79–2.84 Å), comparable with a Pt-Pt separation of 2.78 Å in the pure metal. The compounds referred to in this paper are not oxides but sulfides. Nevertheless, the Pd-Pd separations are still in a range 3.34–3.37 Å as given in Table 1. The three-dimensional network of the palladium chains in the crystal, each palladium being surrounded by four sulfur atoms in square planar coordination, is considered to play a major role in the metallic conduction. According to the recent work of Doublet *et al.* (29), the $x^2 - y^2$ bands of MPd_3S_4 are substantially

dispersive and there occur strong interactions along the *z* direction via the through-bond σ interactions of the square planar PdS₄ unit of the chains. The short Pd-Pd separation, associated with such possible interactions, should be directly related to the mobility of the electrons. As is seen from Table 1, the Pd-Pd separation decreases from 3.3684 Å for LaPd₃S₄ to 3.3382 Å for EuPd₃S₄. In response to this shortening, the Hall mobility actually significantly increases from $4.27 \times 10^{-4} \text{m}^2\text{V}^{-1}\text{s}^{-1}$ for LaPd₃S₄ to $10.00 \times 10^{-4} \text{m}^2\text{V}^{-1}\text{s}^{-1}$ for EuPd₃S₄ (Table 3). The electrical conductivity of EuPd₃S₄ is close to that of NdPd₃S₄ in spite of about half of carrier concentrations in all temperature range (Fig. 6), which may be because of larger Hall mobility of EuPd₃S₄.

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