New quaternary compounds ANb$_2$PS$_{10}$ (A = Na, Ag) and AuNb$_4$P$_2$S$_{20}$ were synthesized and characterized. The structures of three compounds consist of one-dimensional infinite chains built by [Nb$_2$S$_{12}$] and [PS$_4$] units. Cation atoms are occupied within the van der Waals gap of sulfur atoms between infinite chains to make $-S\cdots M^+\cdots S-$ contacts. There is only one Au atom site and so crystallographically a unit cell contains four equivalent Au atoms in AuNb$_4$P$_2$S$_{20}$. This is only the half of the numbers of Na or Ag atoms in NaNb$_2$PS$_{10}$ or AgNb$_2$PS$_{10}$. The ratio between Nb$_2$PS$_{10}$ matrix vs the cation is, therefore, 1 : 1 for Ag and Na, but it is 2 : 1 for Au. Mixed valency in Au or Nb was expected to balance the charge in the latter compound. The electronic structures calculated based on the extended Hückel tight-binding method show that ANb$_2$PS$_{10}$ (A = Ag, Na) are semiconducting, while AuNb$_4$P$_2$S$_{20}$ is metallic, which is not consistent with the experimental results of these three compounds that all exhibit semiconducting property. The result of calculation suggests that AuNb$_4$P$_2$S$_{20}$ might be a magnetic insulator. Magnetic measurement experiment exactly proved that the compound is a Slater antiferromagnetic material with the Néel’s temperature of 45 K. It is recognized, therefore, that electronic structure analysis is very useful to understand the properties of compounds.

Key Words: Mixed valency, Electronic structure, Magnetic insulator

Electronic Structures of ANb$_2$PS$_{10}$ (A=Ag, Na) and AuNb$_4$P$_2$S$_{20}$

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Received February 28, 2003

Electronic Structure Calculation

Electronic Structures of ANb$_2$PS$_{10}$ (A=Ag, Na) and AuNb$_4$P$_2$S$_{20}$

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Electronic Structure Calculation. Electronic structure
calculations for AuNb₄P₂S₂₀ and ANb₂PS₁₀ (A = Na, Ag) were performed by the extended Hückel method within the framework of tight-binding approximation. Density of states (DOS) were calculated based on the given crystal structure for 396 k-points. The atomic orbital parameters employed in the calculation were the default values in the CAESAR program, which are listed in Table 1.

X-Ray Photoelectron Spectroscopy. XPS spectra for AuNb₄P₂S₂₀ and AgNb₂PS₁₀ had been measured with ESCA 2000 electron spectrometer (VG microtech). Pelletized samples were mounted on an aluminium plate. Nonmonochromatic Al Kα radiation was used as an excitation source (hν = 1486.6 eV). During the measurement, the spectrometer was pumped to a residual pressure of ~10⁻⁹ Torr. The data were taken from fresh samples and also after Ar bombardment on surface of palletized samples. The binding energies of gold and niobium in AuNb₄P₂S₂₀ and AgNb₂PS₁₀ were measured. The 1s binding energy of carbon, 284.6 eV was used as an internal standard.

Electron Transport Measurements. The electrical resistance of a single-crystalline AuNb₄P₂S₂₀ was measured using the four-probe method over the temperature 80-300 K.

Magnetic Susceptibility Measurements. Magnetic susceptibility data were recorded on a MPMS5 magnetometer (Quantum Design Inc.). The calibration was made at 298 K using a palladium reference sample furnished by Quantum Design Inc. The data were collected over a temperature range of 15-300 K at a magnetic field of 5000 G and were corrected for diamagnetism.

### Results and Discussion

Crystal Structure. The structure of a quaternary thio-phosphate AuNb₄P₂S₂₀ is similar to those of ANb₂PS₁₀ (A = Na, Ag) family except cation position within a one-dimensional chain framework. Figure 1(a) and 1(b) show the crystal structures of NaNb₄PS₁₀ and AuNb₄P₂S₂₀, which are projected on the ac-plane. The building blocks of the chains are constructed with [Nb₂S₁₂] and [PS₄] units. In [Nb₂S₁₂], each Nb atom is centered in a distorted bicapped trigonal prism composed of three S₂⁻ anions. The [PS₄] units are attached to make bridges between two [Nb₂S₁₂] units to make the long Nb-Nb pair. (The short Nb-Nb interactions are found in the [Nb₂S₁₂] unit itself). Accordingly, the short and long Nb-Nb interactions depend on whether there is a [PS₄] unit between the metals or not.

Au atoms are occupied on a special position in AuNb₄P₂S₂₀ crystal with inversion symmetry, which is different from in NaNb₄PS₁₀ and AgNb₂PS₁₀ because Na⁺ and Ag⁺ cations occupied in the general positions. Au atoms in AuNb₄P₂S₂₀ are in close contact with S atoms in the range of 2.305(2)-3.774(2) Å. The results of the A-S (A=Na, Ag, Au) bond distances are exactly inverse of the cation sizes; 116 pm, 129 pm, and 151 pm for Na⁺, Ag⁺ and Au⁺, respectively, when the coordination number is six. Au atom can make a strong interaction with S atoms as depicted in Scheme 1.

### Table 1. Atomic Orbital Parameters Used in Extended Hückel Calculations

<table>
<thead>
<tr>
<th>Atom</th>
<th>Orbital</th>
<th>( H_i ) (eV)²</th>
<th>( \zeta_1 )</th>
<th>C₁</th>
<th>( \zeta_2 )</th>
<th>C₂</th>
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<tbody>
<tr>
<td>S</td>
<td>3s</td>
<td>-20.0</td>
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<td>1.0</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>3p</td>
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<td>1.827</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>3s</td>
<td>-18.6</td>
<td>1.75</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3p</td>
<td>-14.0</td>
<td>1.30</td>
<td>1.0</td>
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<td></td>
</tr>
<tr>
<td>Nb</td>
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<td>1.89</td>
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</tr>
<tr>
<td></td>
<td>5p</td>
<td>-6.86</td>
<td>1.85</td>
<td>1.0</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>4d</td>
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<td>4.08</td>
<td>0.6401</td>
<td>1.64</td>
<td>0.5516</td>
</tr>
<tr>
<td>Au</td>
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<td>-10.92</td>
<td>2.602</td>
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<tr>
<td></td>
<td>6p</td>
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<td>2.584</td>
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<tr>
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<td>5d</td>
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<td>6.163</td>
<td>0.64418</td>
<td>2.791</td>
<td>0.53558</td>
</tr>
</tbody>
</table>

²\( H_i = \langle \chi_i | H^{\text{eff}} | \chi_i \rangle, i = 1, 2, 3, \ldots \). The value approximated by valence-state ionization potential.
covalent interaction with S atoms since the energy level of its d-orbital lies close to that of S p-orbital, while the interaction should be weak for Ag atom because of the large energy difference, as briefly shown in Scheme 1. The shortest Au-S(10) contacts at 2.305(2) Å is very close to the linear Au-S contacts found in KAuS, KAuS$_3$, and NaAuS$_2$.\textsuperscript{18-20}

The short and long Nb-Nb interactions are found in ANb$_2$PS$_{10}$ and AuNb$_4$P$_2$S$_{20}$ and the bond lengths are similar to those found in other ternary compounds Nb$_2$PS$_{10}$ and Nb$_4$P$_2$S$_{21}$. The eight Nb-S distances are in the range of 2.466(2) Å-2.624(2) Å with the average bond length of 2.538(2) Å in AuNb$_4$P$_2$S$_{20}$. The average distance of P-S bonds is 2.040(3) Å, which is similar to that of AgNb$_2$PS$_{10}$. There is no notable feature in the Nb-S bond lengths; within error range Nb-S bond lengths are almost the same. In the long run, the different aspects between AuNb$_4$P$_2$S$_{20}$ and ANb$_2$PS$_{10}$ (A=Na, Ag) are the cation-sulfur distance and the number of cations.

The stoichiometry of AuNb$_4$P$_2$S$_{20}$ instead of AuNb$_2$PS$_{10}$ suggests that there might be some higher oxidation states on Au atom or other elements such as Nb atoms. Several Au compounds have been known to show mixed valence states Au$^{3+}$ (d$^8$) and Au$^+$ (d$^{10}$). The geometry for Au$^{3+}$ is square planar, while that for Au$^+$ is linear. Since there is only one crystallographical position on Au with linear S-Au-S structure in AuNb$_4$P$_2$S$_{20}$, the possibility of mixed valence states on Au is excluded. Instead, there might be some mixed valence states on Nb atoms to compensate for the positive charge in the compound. Consequently, (Au$^{1+}$)[(Nb$_2$S$_6$)$_2$]$^{5+}$ (PS$_4$$^{3-}$)$_2$ scheme seems to be a reasonable suggestion to satisfy the charge neutrality.

**XPS Spectra.** XPS experiments were carried out to examine the oxidation state of Au and Nb in AuNb$_4$P$_2$S$_{20}$ and the results are listed in Table 2, 3 and 4. The binding energies at 84.4 eV and 88.0 eV are typical indications for Au 4f$^{7/2}$ and 4f$^{5/2}$, respectively, when the Au is mono-positive.\textsuperscript{21} (see Fig. 2). Any indication of Au$^{3+}$, whose peak is typically shown at $>90$ eV is not found. In the long run all Au in AuNb$_4$P$_2$S$_{20}$ can be assigned to be Au$^+$. Figure 3 and 4 show Nb 3d level XPS spectrum of AgNb$_2$PS$_{10}$ and AuNb$_4$P$_2$S$_{20}$, respectively. The Nb 3d level XPS spectrum of AgNb$_2$PS$_{10}$ show doublet at 203.4 eV and 206.2 eV indicating Nb$^{4+}$.\textsuperscript{22} However, the XPS of AuNb$_4$P$_2$S$_{20}$ shows three peaks indicating more than one Nb oxidation state. Since there are two crystallographically different Nb atoms, the oxidation states of the two Nb atoms can be different. The three peaks could be resolved into two pair of Nb 3d$^{5/2}$ and 3d$^{3/2}$ curves of Nb$^{4+}$, and the solid line is the amount of fitted curves.

**Electronic Structure.** Projected density of states (PDOS) calculated for AgNb$_2$PS$_{10}$ and AuNb$_4$P$_2$S$_{20}$ are shown in...
Figure 4. Nb 3d X-ray photoelectron spectrum for AuNb\textsubscript{4}P\textsubscript{2}S\textsubscript{20}. The dashed lines are the fitted 3d\textsubscript{3/2} and 3d\textsubscript{5/2} curves of Nb\textsuperscript{5+}, the dotted lines are those of Nb\textsuperscript{4+}, and the solid line is the amount of fitted curves.

Figure 5(a) and 5(b), respectively. AgNb\textsubscript{2}P\textsubscript{2}S\textsubscript{10} and AuNb\textsubscript{4}P\textsubscript{2}S\textsubscript{20} are semiconducting and metallic, respectively. PDOS data supports the existence of mixed valence not in Au but in Nb. All Au 5d-orbital lies well below the Fermi level, but Nb 4d-orbital lies below and above the Fermi level, which means that the oxidation states of Au and Nb are +1, and +5, respectively. Rather strong interaction of Au-S is supposed to be the reason why the charge transfer occurs from Nb to Au through the Nb-S-Au contact. Electrons move from Nb 4d to Au 5d since the energy level of Nb 4d is higher than that of Au 5d. Consequently, the mixed valency occurs on Nb (i.e., Nb\textsuperscript{4+} and Nb\textsuperscript{5+}) but not on Au (i.e., Au\textsuperscript{5+}) in AuNb\textsubscript{4}P\textsubscript{2}S\textsubscript{20}. This result is consistent with the XPS and crystallographical data.

Figure 6. (a) Electrical resistivity data of AuNb\textsubscript{4}P\textsubscript{2}S\textsubscript{20} as a function of temperature and (b) that for AgNb\textsubscript{2}P\textsubscript{2}S\textsubscript{10}.

Electron Transport and Magnetic Properties. The temperature dependency of the electrical resistivity for AuNb\textsubscript{4}P\textsubscript{2}S\textsubscript{20} is shown in Figure 6. The temperature dependency of the electrical resistivity for AgNb\textsubscript{2}P\textsubscript{2}S\textsubscript{10} and NaNb\textsubscript{2}P\textsubscript{2}S\textsubscript{10} show similar pattern so those are not shown. All showed semiconducting behavior which is not consistent with the result of DOS calculated for AuNb\textsubscript{4}P\textsubscript{2}S\textsubscript{20}. The metallic property from the DOS in AuNb\textsubscript{4}P\textsubscript{2}S\textsubscript{20} might be due to the shortage of electrons donated by the cation (i.e., see the stoichiometries of AuNb\textsubscript{4}P\textsubscript{2}S\textsubscript{20} and AgNb\textsubscript{2}P\textsubscript{2}S\textsubscript{10}). In the metallic figure, the valence band of AuNb\textsubscript{4}P\textsubscript{2}S\textsubscript{20} consists of mainly Nb d-orbital with the d\textsuperscript{4} or d\textsuperscript{5} electronic configuration according to the mixed valency on Nb. It is well established that the electronic state of a crystalline solid with a partially filled band may not become metallic but insulating so as to minimize electron-electron repulsion (see Scheme 2). Such an insulating state can be magnetic or nonmagnetic depending upon how electron-electron repulsion is minimized. For

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Scheme 2
instance, a magnetic insulating state of the Slater antiferromagnetism introduces spin density alternation at neighboring sites, thus decreasing the on-site electron-electron repulsion. To understand the difference the results of between electronic structure calculation and electron transport measurement, magnetic measurements was performed. The discrepancy between the calculated and experimental results suggests that the compound might be a magnetic insulator. The magnetic susceptibility data in Figure 7 clearly show that AuNb₄P₂S₂₀ illustrates ferromagnetic and antiferromagnetic properties with the Neels’ temperature (T_N) of 45 K. It is recognized, therefore, that electronic structure analysis is very useful to understand the properties of compounds.

Acknowledgments. D. Jung acknowledges financial support from wonkwang university in the year of 2002.

References