The Relationship between the Eh-pH Diagram for the Pb-S-H$_2$O System and Semiconducting Properties of Galena

Hiroshi Kametani* and Mikihiko Kobayashi*

Abstract: The partial pressure of sulfur is an important factor in the equilibria of metal sulfide systems, the genesis of ore deposits, and in the preparation of sulfide semiconductors. Thermoelectric power, which is one of the semiconducting properties, can easily be measured by using particulate mineral samples. Therefore, an Eh-pH diagram, in which semiconducting properties could be predicted on the stable region for the metal sulfide, would be very useful. Such a diagram was constructed for the Pb-S-H$_2$O system at 200°C (473 K) by introducing isobaric curves of the partial pressure of sulfur obtained from the vapour pressure of elemental sulfur, and by extrapolating reported data for preparation of semiconducting PbS at high temperatures to 200°C. It was shown that the stable region for undoped PbS on the diagram involved two regions for p- and n-type PbS. Measured values of thermoelectric power for particulate galena samples were briefly described. It was shown that galena samples from the kuroko-type ore deposits were p-type semiconductors, whereas those from the other vein- and skarn-type ore deposits were n-type.

Introduction

The semiconducting properties of a sulfide mineral are generally measured using a specimen cut from a mineral crystal free from defects. Particulate samples of sulfide minerals have been used for measurements of thermoelectric power (KAMETANI, 1982). The advantages of particulate samples are that they can easily be obtained from either granular, brittle lump, or polycrystalline ores, and that only about 0.7 g of the sample is required. Measurements of particulate samples of a yellow ore from the Matsumine deposit of kuroko-type have shown that there is continuous variation in thermoelectric power with the location of sampling (KAMETANI and KOBAYASHI, 1985). Such variations, and more generally "iso-thermoelectric power-faces", may be closely related to the formation of the ore deposit.

Eh-pH diagrams predict equilibria among the species involved and are widely used in mineralogical considerations (GARRELS and CHRIST, 1965, p. 379~400). The partial pressure of sulfur is an important parameter when considering the formation of ore deposits, however conventional diagrams do not display the isobaric curves of sulfur vapour. The partial pressure of sulfur also plays an important role in determining the electronic nature of metal sulfide semiconductors. For example, PbS semiconductors having various properties are prepared under controlled sulfur pressure. It seems, therefore, that semiconducting properties can be predicted on an Eh-pH diagram by taking account of the partial pressure of sulfur. This diagram would, together with the thermoelectric power measurements, allow detailed discussion of the genesis of ore deposits.

1. Construction of Eh-pH Diagram at 200°C

WATANABE (1973) has summarized reported values of the temperature of formation for kuroko-type ore deposits and recommended the temperatures obtained by the sulfur isotope geothermometer. They are: black ore 230°C~300°C (503~573 K), yellow ore 260°C~310°C (533~583 K), silicious ore 270°C~360°C (543~633 K). Thus, it can be seen that...
the sulfide minerals in these deposits are formed in the temperature range from 230° to 360°C (503–633 K).

Thermodynamic values of the standard energy of formation, $\Delta G^\circ$, used for construction of the Eh-pH diagram for the Pb–S–H₂O system were taken from data by YAZAWA and EGUCHI (1975, p. 12). Values at 100°, 200°, and 300°C were calculated by the entropy correspondence principle (CRISS and COBBLE, 1964). Because some of the data at 300°C was missing, the diagram was constructed for 200°C (473 K), which was slightly lower than the mineralization temperature described above.

SHIKAZONO (1976) has estimated compositions of ore solution involved in the formation of kuroko-type ore deposits. It was shown that the concentrations of H₂S, SO₄²⁻, and metal ions (Pb, Zn, Cu, and Fe) were in the range from 20–1150 ppm, 0.0–3600 ppm, and 0.01–220 ppm, respectively. For the purpose of calculation, total activity of dissolved sulfur species was assumed to be 10⁻⁴ and that of dissolved Pb species 10⁻⁶ as approximation.

The partial pressure of S₂ in equilibrium with molten sulfur, $P_{S_2}$, was calculated from data by KUBASCHEWSKI and ALCOCK (1979, p. 370) as given by

$$ log P_{S_2} (\text{mmHg}) = \frac{-6975}{T} - 1.53 \log T - 10^{-3} T + 16.22 $$

for 119°C (m.p.)–444.6°C (b.p.) (1)

where $T$ is the absolute temperature. Equation (1) yields,

$$ log P_{S_2} (\text{mmHg}) = \frac{-6975}{T} - 5.0 \log T + 23.88 $$

for 119°C (m.p.)–444.6°C (b.p.) (2)

and

$$ P_{S_2} (\text{atm}) = 1.09 \times 10^{-6} \ \text{at} \ 200^\circ\text{C} (1') $$

For comparison, the total pressure of sulfur (S₂–S₈) in equilibrium with molten sulfur, $P_{S_2}$, is given by

$$ log P_{S_2} (\text{mmHg}) = \frac{-4830}{T} - 5.0 \log T + 23.88 $$

for 119°C (m.p.)–444.6°C (b.p.) (2')

and

$$ P_{S_2} (\text{atm}) = 2.62 \times 10^{-3} \ \text{at} \ 200^\circ\text{C} (2') $$

On the Eh-pH diagram for the S–H₂O system (total activity of dissolved sulfur species: 10⁻⁴) at 200°C, the stable region of elemental sulfur exists below pH = –6.35. On

![Fig. 1 Eh-pH diagram for the S–H₂O system showing the isobaric curves of S₂ (g). Calculated at 200°C in the pH range from 0 to 12 and total activity of soluble sulfur species: 10⁻⁴.](image-url)
the boundary lines for \( S/H_2S \) and \( HSO_4^-/S \), \( P_{S_2} \) should be equal to the pressure given by Equation (1'). The value of \( (RT/F) \ln a \) amounts to 0.09388 log \( a \) at 200°C, where \( R, F, \) and \( a \) are the gas constant, Faraday constant, and activity, respectively. Calculated values of \( \Delta G^\circ \) and potential equations for reactions involved in the S–H_2O system are shown in Table 1.

Constructed Eh-pH diagram which involves isobaric curves of different \( P_{S_2} \) in the pH range from 0 to 12 is shown in Figure 1.

2. Semiconducting Properties of PbS

2.1 Semiconducting properties of PbS

Galena is the most famous semiconductor among sulfide minerals and semiconducting properties of undoped and doped PbS have been studied in detail. Therefore, basic considerations on the semiconducting properties are made referring data of PbS to give information for the other minerals.

The carrier concentrations of undoped PbS are highly dependent on the deviation from the stoichiometric composition. In order to prepare a PbS sample having a desired carrier concentration, the sample is first heated in a gas with a proper \( P_{S_2} \) for sufficient time to establish equilibrium by diffusion, and then it is quenched. BREBRICK and SCANLON (1954) studied the equilibrium between PbS crystals of 2 mm thickness and \( P_{S_2} \) at 500°C (773 K). BLOEM, et al. (1955) and BLOEM (1956) proposed the theory of valency control for doped PbS. SCANLON (1959) described a review on semiconducting properties of Pb chalcogenides (S, Se, Te), and gave a log \( P_{S_2} \) vs. 1/T diagram showing the variation of carrier concentrations and the boundaries between p- and n-type regions for undoped PbS.

At a given temperature, the concentration of electrons, \( \left( e^- \right) \), and of positive holes, \( \left( h^+ \right) \), of undoped PbS vary in proportion to \( P_{S_2}^{1/4} \) (BLOEM, 1956) as given by

\[
\begin{align*}
\left( e^- \right) & \propto P_{S_2}^{1/4} \quad (8) \\
\left( h^+ \right) & \propto P_{S_2}^{1/4} \quad (9)
\end{align*}
\]

As a result, there is a critical value of \( P_{S_2}, P_c \), at which \( \left( e^- \right) \) is roughly equal to \( \left( h^+ \right) \) as shown in the schematic illustration, Figure 2. \( P_c \) gives the boundary between p- and n-type semiconductors. For \( P_{S_2} > P_c \), \( \left( h^+ \right) \) is higher than \( \left( e^- \right) \) and the PbS behaves as p-type semiconductor, whereas for \( P_{S_2} < P_c \), \( \left( e^- \right) \) is higher than \( \left( h^+ \right) \) and the PbS is n-type. The former is the case of sulfur excess and the latter is metal excess. The value of \( P_c \) varies with the temperature and with the concentration of doped impurities, see Figure 2.

To attain rapid rates of diffusion, the preparation of semiconductor PbS is usually carried out at temperatures above 500°C, and semiconducting properties have been measured for samples quenched from these temperatures. Thus, in order to estimate the carrier concentration at 200°C, it was necessary to extrapolate data obtained at higher temperatures. This was achieved by assuming a linear dependence of log \( P_{S_2} \) upon 1/T. Using data obtained by BLOEM (1956) in the temperature range from 900~1200 K, the variation of \( P_c \) with temperature for undoped PbS was calculated as follows.

\[
\log P_c = 4.64 - \frac{7200}{T}
\]

for undoped PbS (10)

Doped PbS behaves as undoped PbS above a high temperature which depends upon the concentration of doped impurity. In a temperature range below this temperature, the dependence of log \( P_{S_2} \) upon 1/T is not linear, however it becomes again nearly linear at sufficiently low temperatures. Assuming the linear dependence below about 900 K, the following equations were obtained for doped PbS.

\[
\log P_c = 20.60 - \frac{2260}{T}
\]

for Ag (10^{17} cm^{-3}) doped PbS (11)
Table 2 Calculated values of the partial pressure of \( S_2 \) for boundaries and carrier concentrations at 200°C (473 K)

<table>
<thead>
<tr>
<th>Condition</th>
<th>No. of equation</th>
<th>( \log P_{c} ) by Bloem (1956)</th>
<th>( \log P_{c} ) by Scanlon (1959)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped PbS</td>
<td>Boundary for S/PbS</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>((h^+)=10^{18}\ \text{cm}^{-3}) (p-type)</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Boundary between p- and n-types ((P_c))</td>
<td>10, 15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>((e^-)=10^{18}\ \text{cm}^{-3}) (n-type)</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Boundary for PbS/Pb</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Doped PbS</td>
<td>Boundary between p- and n-type ((P_c))</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>for Ag ((10^{17}\ \text{cm}^{-3})) doped PbS</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Boundary between p- and n-types ((P_c))</td>
<td>12</td>
<td>3.39</td>
</tr>
<tr>
<td></td>
<td>for Bi ((10^{17}\ \text{cm}^{-3})) doped PbS</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ \log P_{c} = -9.15 + \frac{5930}{T} \]

for Bi \((10^{17}\ \text{cm}^{-3})\) doped PbS \ (12)

A phase diagram for the PbS system given by Scanlon (1959) gave

\[ \log P_{S_2} = 4.53 - \frac{3360}{T} \]

for the boundary S/PbS \ (13)

\[ \log P_{S_2} = 1.80 - \frac{3560}{T} \]

for \((h^+)=10^{18}\ \text{cm}^{-3}\) p-type \ (14)

\[ \log P_{c} = 4.96 - \frac{7640}{T} \]

for \((h^+)=<e^->\) \ (15)

\[ \log P_{S_2} = 9.34 - \frac{13510}{T} \]

for \((e^-)=10^{18}\ \text{cm}^{-3}\) n-type \ (16)

\[ \log P_{S_2} = 8.77 - \frac{16290}{T} \]

for the boundary PbS/Pb \ (17)

Values of \( P_{S_2} \) and \( P_{c} \) at 200°C calculated from Equations (10) to (17) are listed in Table 2. There found a slight difference between the values of \( P_{c} \) calculated from Bloem’s (1956) and Scanlon’s (1959) data. This difference may be due to the extrapolation procedure, however the difference seems to be allowable error. Therefore, the value by Scanlon, \( \log P_{c} = -11.19 \) is used for undoped PbS. The other calculated values may also contain more or less the same magnitude of error as the difference in \( P_{c} \), however they are valid as approximation. More experimental work is clearly required to corroborate the estimated values.

2.2 Carrier concentration predicted on the Eh-pH diagram

The Eh-pH diagram for the Pb-S-H2O system was constructed as described above and isobaric curves of \( P_{S_2} \) and \( P_{c} \) in Table 2 were predicted on the diagram, Figure 3. The boundary between the S and PbS regions does not appear on the figure and that between the PbS and Pb regions calculated from the \( P_{S_2} \) data lie slightly apart from that calculated from the thermodynamic data. The discrepancy is small however and probably results from the extrapolation.

The variation of the carrier concentrations with \( P_{S_2} \) may be calculated using the data in Table 2 and Equations (8) and (9):

\[ \log (h^+) = 19.43 + 0.25 \log P_{S_2} \]

(18)

\[ \log (e^-) = 13.19 - 0.25 \log P_{S_2} \]

(19)

\[ \log P_{c} \] for Ag doped PbS was calculated to be \(-27.18\) (Table 2). This is nearly on the boundary between the PbS and Pb regions \((\log P_{S_2} = -25.66)\), which means that Ag doped PbS always behaves as p-type. On the other hand, \( \log P_{c} \) of Bi doped PbS is very high \((\log P_{S_2} = 3.39)\), and the PbS always behaves as n-type.

With regard to the formation of PbS, Figure 3 shows that n-type PbS can form over a wide range of pH and \( P_{S_2} \), in consequence the potential, and would be expected to predominate over the p-type which can exist over a much smaller range of conditions. This figure also shows that the isobaric line for \( P_{c} \)
The relationship between the Eh-pH diagram for the Pb-S-H₂O system

Table 3 Calculated time required to establish the equilibrium by diffusion

<table>
<thead>
<tr>
<th>D₀⁺</th>
<th>Eᵃ</th>
<th>D₉₀₀⁺</th>
<th>Calculated duration h</th>
<th>Calculated at 200°C (473 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 × 10⁻²</td>
<td>7.58</td>
<td>1.5 × 10⁻⁶</td>
<td>5</td>
<td>8 × 10⁻⁸</td>
</tr>
<tr>
<td>2</td>
<td>23.0</td>
<td>0.81 × 10⁻⁶</td>
<td>9.3</td>
<td>5 × 10⁻¹¹</td>
</tr>
<tr>
<td>2 × 10²</td>
<td>30.3</td>
<td>0.61 × 10⁻⁶</td>
<td>12.3</td>
<td>2 × 10⁻¹²</td>
</tr>
</tbody>
</table>

Experimental 20

*"D=D₀ exp (-(E/RT)). Data from BREBRICK and SCANLON (1954), Degree of conversion: 99.8%.

Fig. 3 Eh-pH diagram for the Pb-S-H₂O system showing stable regions for p- and n-type undoped PbS and carrier concentration (cm⁻³, dotted line) by means of isobaric curves of S₂ (g) (broken lines). Calculated at 200°C for activities of soluble sulfur and Pb species of 10⁻⁴ and 10⁻⁶, respectively.

(Equation (15)) intersects the boundary between the Pb²⁺ and PbS regions at pH = 3.33. Between pH = 3.19 and 3.33, p-type PbS would form from solution, whereas above pH = 3.33, n-type PbS would be stable.

2.3 Time required to establish the equilibrium

BREBRICK and SCANLON (1954) calculated the time required to establish equilibrium between the gas phase and a PbS specimen with a thickness of 2 mm. For the diffusion of a change in composition, the calculated values of the time at 500°C ranged from 5 to 12.3 h (Table 3). These values may be compared with the 20 h found by their experiment. The time varies somewhat for different PbS crystals. Using Brebrick and Scanlon's data, the diffusion coefficient at 200°C, D₂00, the ratios D₉₀₀/D₂₀₀, and the equilibration time were estimated (Table 3). The calculations show that when the activation energy is high (e.g., 30.3 kcal/mol), the equilibration time at 200°C may amount to 150,000 days, about 400 years. Assuming that the root of the equilibration time is proportional to the thickness, the time for a small 10 μm crystal may be reduced to 20 h, which is the same as the time required for a large 2 mm crystal at the high temperature.

3. Thermoelectric Power of Galena

3.1 Variation of thermoelectric power of PbS with temperature

BLOEM (1956) gave empirical relations between the thermoelectric power, \( \alpha (\mu V/K) \) and the carrier concentrations (cm⁻³) for PbS. The specimens were prepared by equilibration at high temperatures, followed by quenching. The relations are given by

\[ \alpha = -200 (19.4 - \log n) \]

for n-type (20)

\[ \alpha = 200 (19.4 - \log p) \]

for p-type (21)

where \( n \) and \( p \) are the carrier concentrations of electrons and holes, respectively, in the range from about 10¹⁷ to 10¹⁹ cm⁻³.

Using the experimental values of carrier concentrations reported by SCANLON (1959) and BLOEM (1956) and Equations (20) and (21), the variation of thermoelectric power with the equilibration temperature at a constant log \( P₅,₂ \)
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Fig. 4 Schematic illustration showing the variation of thermoelectric power of undoped and doped PbS with the temperature at a constant pressure, $P_S = 10^{-3}$ atm. Data from SCANLON (1959, white circle) and BLOEM (1956, black circle). PbS specimens were equilibrated at each temperature and then quenched.

of $-3$ is estimated and shown in Figure 4. $\alpha$ for undoped PbS at low temperatures is around $+300 \mu V/K$. It changes rapidly from the positive value to $-300 \mu V/K$ at about $1000 K$ at which the boundary for $p-n$ transition lies, and finally approaches a value of $-30 \mu V/K$ at about $1330 K$, which corresponds to the decomposition temperature of PbS at $\log P_S = -3$. The behaviour of Ag doped PbS resembles that of undoped PbS, however the curve shifts to the high temperature side. At low temperature, the effect of Bi impurity is to lower the value of $\alpha$ which changes its sign and shows a low value of about $-400 \mu V/K$ at about $1000 K$. At high temperatures all curves for doped PbS agree with that for undoped PbS.

3.2 Thermoelectric power measurements of galena

Semiconducting properties are generally measured using solid specimens cut from mineral crystals. It is difficult, however, to obtain natural crystals that are free from defects and cracks, and such measurements would be much easier if particulate samples could be used. In most electrical measurements, the contact resistance between particles is a major problem, but in the case of thermoelectric power measurements, which do not involve the passage of a current, this problem does not arise.

The original (KAMETANI, 1982) and subsequently improved versions (KAMETANI and KOBAYASHI, 1985) of the apparatus for thermoelectric power measurement have been described elsewhere. Briefly, about 0.7 g of a particulate sample is placed in a $6 \text{ mm I.D.}$ vertical quartz tube to form a packed bed located between two titanium cups. One upper cup is in contact with an upper thermocouple, and the lower other with a lower thermocouple. The packed bed is compressed by loading with a weight. Argon gas is introduced into the tube at a small flow rate to prevent oxidation of the sample during the measurement.

The packed bed is subjected to a small temperature gradient, $\Delta T$ (degree, K), generated by a small cylindrical heater placed around the outside of the tube. The variations of thermo-emf, $\Delta E$ (µV), with $\Delta T$ are measured at different $\Delta T$'s. From the linear relation between $\Delta E$ and $\Delta T$, the thermoelectric power, $\alpha$ (µV/K) is calculated as follows.

$$\alpha = -\frac{\Delta E}{\Delta T}$$

(22)

Here, the thermoelectric power of the metal lead wires is assumed to be negligibly small.

Particulate samples were prepared by gently crushing massive lumps and sieving. Some were prepared by picking or cleaving crystalline particles from granular samples. Results of the measurements for galena samples are shown in Table 4. It can be seen that values of $\alpha$ for crystalline samples are in reasonable agreement with those measured for the particulate samples. The four galena samples from the hydrothermal ore deposits were aggregate lumps of small crystalline galena and were all $n$-type, the values of which fell in the range from $-99$ to $-323 \mu V/K$. On the other hand, the two samples from the kuroko-type ore deposits were $p$-type semiconductors. The latter two samples were fine
The relationship between the Eh-pH diagram for the Pb-S-H₂O system...

Table 4 Measured values of thermoelectric power for galena samples from different mines

<table>
<thead>
<tr>
<th>Mine</th>
<th>Type of ore deposit</th>
<th>Size</th>
<th>Thermoelectric power (type) μV/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kamioka</td>
<td>Skarn-type</td>
<td>250–710 μm</td>
<td>-317 (n)</td>
</tr>
<tr>
<td>Motokura</td>
<td>Hydrothermal</td>
<td>Crystal, 2.8 × 3.1 × 1.4 Hmm ca. 1 mm (pick up)</td>
<td>-280 (n)</td>
</tr>
<tr>
<td>Hosokura</td>
<td>Vein-type</td>
<td>Crystal, 2.1 × 2.7 × 1.1 Hmm 250–710 μm</td>
<td>-258 (n)</td>
</tr>
<tr>
<td>Budo</td>
<td>Vein-type</td>
<td>250–710 μm</td>
<td>-245 (n)</td>
</tr>
<tr>
<td>Matsumine</td>
<td>Kuroko-type</td>
<td>250–710 μm</td>
<td>-99 (n)</td>
</tr>
<tr>
<td>Ezuri</td>
<td>Kuroko-type</td>
<td>250–710 μm</td>
<td>265 (ρ)</td>
</tr>
</tbody>
</table>

Fig. 5 Correlation between the thermoelectric power, α, and the chalcopyrite (Cp) content for PbS samples. Galena samples: 1 Matsumine, 2 Ezuri. Pb concentrates: A Uchinotai, B Matsumine, C Fukazawa, D Furutobe, E Hanawa, and F Shakanai. Black circles: Pb concentrates from the Fukazawa mine (KAMETANI and KOBAYASHI, 1984).

The effect of these contaminant minerals on the semiconducting properties of the samples is not fully understood. KAMETANI and KOBAYASHI (1984) demonstrated that thermoelectric power for galena and Pb concentrates from kuroko-type ore deposits varied with the chalcopyrite content as shown in Figure 5. It can be seen that α was practically independent of chalcopyrite content until it reached 10 mol%, after which there was a sharp drop in thermoelectric power.

Chalcopyrite does not dissolve in galena. The samples used may contain fine inclusions of chalcopyrite dispersed in a matrix of galena. Particulate samples of chalcopyrite obtained from the Shakanai mine were reported to be n-type semiconductors with values of α ranging from -35 to -381 μV/K (NISHIYAMA, 1984). The n-type behaviour of chalcopyrite inclusions seems to appear only above the critical content of 10 mol%. The sharp drop might be due to the electronic interaction between the inclusions and the matrix of galena.

MINO and Saito (1959) measured Hall coefficients for several galena samples from various locations in Japan. They pointed out that the carrier concentration increased with the Ag content (Table 5). Five out of seven of the samples were n-type semiconductors. Values of α calculated from the carrier concentrations are listed in Table 5. Figure 6 shows the linear correlation between |α| and the Ag content which is expressed by the following equation.

\[ |\alpha| (\muV/K) = 1556 - 448 \log C_{Ag} \]  

(23)

where \(C_{Ag}\) is the Ag content in g/t. Equation (23) can be re-arranged to give,
Table 5 Data (Mino and Saito, 1959) for carrier concentrations for galena and calculated values of thermoelectric power

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type of ore deposit</th>
<th>Ag content, g/t</th>
<th>Bi content, g/t</th>
<th>Carrier concentration, cm⁻³</th>
<th>Type</th>
<th>Calculated thermoelectric power, µV/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asahi</td>
<td>Kuroko-type</td>
<td>196</td>
<td>tr</td>
<td>1.1 x 10⁻¹⁷</td>
<td>p</td>
<td>472</td>
</tr>
<tr>
<td>Budo</td>
<td>Vein-type</td>
<td>318</td>
<td>450</td>
<td>5.6 x 10⁻¹⁶</td>
<td>p</td>
<td>530</td>
</tr>
<tr>
<td>Mozumi*</td>
<td>Skarn-type</td>
<td>436</td>
<td>tr</td>
<td>1.3 x 10⁻¹⁷</td>
<td>n</td>
<td>-458</td>
</tr>
<tr>
<td>Daira</td>
<td>Vein-type**</td>
<td>476</td>
<td>200</td>
<td>8.1 x 10⁻¹⁷</td>
<td>n</td>
<td>-298</td>
</tr>
<tr>
<td>Tochibora*</td>
<td>Skarn-type</td>
<td>630</td>
<td>700</td>
<td>3.1 x 10⁻¹⁷</td>
<td>n</td>
<td>-382</td>
</tr>
<tr>
<td>Oppu</td>
<td>Vein-type**</td>
<td>1565</td>
<td>2500</td>
<td>6.4 x 10⁻¹⁸</td>
<td>n</td>
<td>-118</td>
</tr>
<tr>
<td>Taro</td>
<td>Kieslager</td>
<td>2048</td>
<td>100</td>
<td>8.7 x 10⁻¹⁸</td>
<td>n</td>
<td>-92</td>
</tr>
</tbody>
</table>

*Kamioka Mine, **metamorphed.

\[ |\alpha| \text{ (V/K)} = 1.56 \times 10^{-3} - 4.5 \frac{k}{2e} \ln C_{Ag} \]  
\( (24) \)

where \( e \) is the charge of an electron and \( k \) is Boltzmann’s constant.

According to the theoretical equation for a simple \( n \)-type impurity semiconductor in which the carrier concentration is controlled by the donor (Kobayashi, 1957, p. 145–50), the variation of \( \alpha \) with the carrier concentration, \( N_D \), is given by

\[ \alpha \propto \frac{k}{2e} \ln \left( \frac{N_D}{N_C} \right) \]  
\( (25) \)

where \( N_C \) is a constant. The coefficient 4.5 in Equation (24) is roughly comparable with the value of 1 in Equation (25).

If the presence of Ag is ignored, the predominance of \( n \)-type samples in Table 5 agrees with the Eh-pH diagram shown in Figure 3, in which the \( n \)-type region is much larger than the \( p \)-type region. However, Figure 6 suggests that there is a correlation between \( \alpha \) and the Ag content. This correlation does not agree with the previous observation that Ag doped PbS behaves as a \( p \)-type semiconductor. This discrepancy is difficult to explain at present, however some suggestions can be made from the data as follows.

The carrier concentrations shown in Table 5 are of the order of \( 10^{17} \sim 10^{19} \) cm⁻³, which corresponds to 2.4–240 g/t of Ag in galena. It seems that these low values are out of balance with the higher Ag contents which range from 200 to 2000 g/t.

The solubility limit of Ag in galena in the uniform phase is found to be about 1000 to 1700 g/t (Mino and Saito, 1958), and these high values suggest that the Ag may exist as dissolved \( \beta \)-Ag₃S (argentite). In the presence of Bi (Table 5), Ag tends to form \( \alpha \)-AgBiS₂ (matildite), a part of which may exist in galena as solid solution, while the excess is deposited to form fine inclusions (Mino and Saito, 1958). It is known that \( \beta \)-Ag₃S is an \( n \)-type semiconductor (Kawaguchi, 1974, p. 27–30). Although there is no data for \( \alpha \)-AgBiS₂, it seems reasonable to suppose that this sulfide mineral may also behave as an \( n \)-type semiconductor when the partial pressure of sulfur is
low. It follows that the contaminated galena would behave as an n-type semiconductor if the dissolved n-type minerals controlled the semiconducting properties as a whole.

It may seem wrong to compare Equation (23), which is obtained from the empirical correlation in Figure 6, with Equation (25), which is derived from the valency control mechanism. However, the theory of valency control is well established and has been widely applied to predict the effect of controlled doping of impurities. On the other hand, little is known about the complicated effects of various contaminants in natural sulfide minerals. The rough correspondence between Equations (24) and (25) might be coincidental, alternatively it might show a phenomenological resemblance between the effects of controlled doping and of a secondary mineral as solid solution and/or as dispersed inclusions.

It has been found that the variation of $\alpha$ with the chalcopyrite content in pyrite is represented by

$$\alpha = 160 - 300 \log C_{Cp}$$  \hspace{1cm} (26)

where $C_{Cp}$ is the chalcopyrite content in the range from 1.5 to 20 mol\% (KAMETANI and KOBAYASHI, 1984). The value of 300 in Equation (26) is apparently comparable with 448 in Equation (23). In this case, chalcopyrite may exist as inclusions in pyrite. A closely controlled study of the effect of impurities, and further accumulation of detailed data for natural sulfide minerals, would be most rewarding.

### 4. Application of Eh-pH Diagram and Thermoelectric Power Measurement

The formation of Neogene ore deposits in Japan occurs by two main processes. The one is the deposition of minerals from ore solution under volcanic conditions and the other is submarine spouting of metal sulfides. Large mineral crystals may often be formed by the former process, while sedimentation of very fine sulfide particles takes place in the latter. Over a long period of time, the primary ore deposit may undergo various secondary changes such as recrystallization, reconstruction, metasomatism, and metamorphism. Thus, the nature of a mineral sample is dependent upon either the conditions under which it was formed, or those of the latest secondary change which took place. The history of a mineral sample can be investigated by means of mineralogical, geological, chemical, and physical examinations and equilibrium analysis. Semiconducting properties are also a useful means for detecting minute differences between samples.

This paper presents an Eh-pH diagram involving the semiconducting properties of galena for fundamental consideration, and also the thermoelectric power data of particulate gallena samples for comparison. The particulate sample required for the measurement can be obtained much more easily than the natural mineral crystal. This allows examination of, for instance, variation along the direction of a vein, iso-thermoelectric power-faces in an ore deposit, and correlations among ore deposits and among mines. These examinations would be invaluable in considerations of the formation and development of ore deposits.

At present, few data on the semiconducting properties of galena have been obtained. The Eh-pH diagram should be constructed more precisely and tested by further experimentation. Measured values of the thermoelectric power in Tables 4 and 5 reveal that there is an apparent difference in semiconducting properties between the galena samples obtained from the skarn- and vein-type ore deposits, and those from the kuroko-type ore deposits. Table 5 also shows that most of the n-type samples were from skarn- and vein-type ore deposits, and those from the kuroko-type ore deposits. It seems likely that the kuroko-type ore deposit may have been formed at higher Eh than the skarn- and vein-type ore deposits, if Figure 3 can be used. Differences were also found between samples taken from different locations in the same mine. The two samples from the Budo mine were of different types: the one in Table 4 was an n-type, while the other in Table 5 was a p-type.

When ore deposits contain various sulfide minerals, it may be assumed that the condi-
Fig. 7 Stable regions for chalcopyrite, pyrite, pyrrhotite, galena, and sphalerite on the Eh-pH diagram. Calculated at 200°C for activities of soluble sulfur and metal species of 10^{-4} and 10^{-6}, respectively.

Assuming equilibria among the minerals and in the absence of electronic interaction, coexistence of $p$-type galena and chalcopyrite is possible in the upper left-hand side of the stable region for galena. Complex sulfide minerals (kuroko) containing chalcopyrite, pyrite, galena, and sphalerite may be formed in the smallest region for pyrite.

**Conclusion**

Eh-pH diagrams for the S-H_{2}O and Metal-S-H_{2}O systems were constructed for the activities of soluble sulfur and metal species of 10^{-4} and 10^{-6}, respectively, at 200°C (473 K). Values of the partial pressure of S_{2} (g) were calculated for the equilibria between elemental sulfur and dissolved H_{2}S, and between that and HSO_{3}^{-}. The values of the partial pressure of S_{2} were displayed as isobaric curves on the Eh-pH diagram. Reported data on the partial pressure of S_{2} for the preparation of semiconducting PbS at high temperatures was extrapolated to 200°C.

For undoped PbS, the stable region of PbS on the diagram was divided into two regions by the boundary between $p$-type and $n$-type PbS. The $p$-type region was wedge-shaped and surrounded by the larger $n$-type PbS region. It was shown that Ag doped PbS was always $p$-type, whereas Bi doped PbS was always $n$-type.

Thermoelectric power is one of semiconductor properties. A method for measuring thermoelectric power in particulate samples was briefly described. Several measured values of thermoelectric power for natural galena samples were presented and it was shown that the samples from the kuroko-type ore deposits were $p$-type semiconductors, whereas those from the skarn- and vein-type ore deposits were $n$-type. It was suggested that the former was formed at higher Eh than the latter. Further experimental work is required to extend these studies.

**References**

The relationship between the Eh-pH diagram for the Pb–S–H₂O system

Econ. Geol., 61, 518–49.


Pb–S–H₂O 系電位–pH 図と PbS の半導体的性質の関係

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要旨：Metal–S–H₂O 系の電位–pH 図にて，金属硫化物の半導体的性質を表すことができれば，鉱床の成因の検討に際して有利となると思われる。PbS 半導体は試片と S 蒸気を高温で拡散平衡させて作成されると，S 蒸気圧（Pₛ）を介して PbS 安定領域内にキャリアーの種類・濃度を示すことができると考えて検討を試みた。

鉱床生成に関連して，200°C (473 K)，S および Pb の可溶性化学種の活量をそれぞれ 10⁻⁴, 10⁻⁶ とし，まず S–H₂O 系電位–pH 図に等 Pₛ 線を記入した。PbS の半導体的性質は，文献値（高溫）より外挿して200°Cの平衡 Pₛ 線を含む Pb–S–H₂O 系電位–pH 図を作製し，平衡 Pₛ を検討した。その結果，ドープしない純 PbS では，その安定領域内の電位の高い所にくさび形の p 型の領域があり，その周りを囲むようにして n 型の領域があることが判明した。全体としてみると n 型 PbS 生成の条件の範囲は p 型 PbS のそれより広く，n 型の方が生成し易いといえる。Ag または Bi をドープした PbS の場合は，PbS の全安定領域がそれぞれ p 型または n 型の PbS になると推定された。

以上のような半導体的性質と電位–pH 図の関係を実証するためには，試料が少量でかつ試料でも測定可能な熱電率が有用と考えられる。しかしこの熱電率についてはあまり知られていないので，文献より計算した PbS の熱電率の温度依存性を模式的に説明した。また粉末試料の熱電率測定法を簡単に述べ，方鉛鉱に関する測定値，計算値を検討した。その結果，黒鉛鉱鉱床中の方鉛鉱は p 型半導体であるが，その他の硫化系などの鉱床中の方鉛鉱は n 型半導体であると推定された。その他，上記の電位–pH 図の応用について簡単に述べた。

Asahi：朝日（福島県）
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Daira：大良（秋田県）
Ezuri：鷹鈴（秋田県）
Fukazawa：深沢（秋田県）
Hosokura：細倉（宮城県）
Kamioka：神岡（岐阜県）
Matsumine：松峰（秋田県）
Motokura：本郷（北海道）
Mozumi：茂住（岐阜県）
Oppu：尾太（青森県）
Taro：田老（岩手県）
Tochibora：橘洞（岐阜県）