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## MAGNETIC AND ELECTRICAL PROPERTIES OF $\text{Co}(\text{As}_x\text{S}_{1-x})_2$ AND $\text{Ni}(\text{As}_x\text{S}_{1-x})_2$

K. ADACHI, E. TOGAWA and F. KIMURA

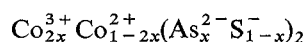
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**Résumé.** — Les propriétés magnétiques et électriques de  $\text{Co}(\text{As}_x\text{S}_{1-x})_2$  ont été étudiées de même que les diagrammes de phase. Dans  $\text{Co}(\text{As}_x\text{S}_{1-x})_2$  la concentration correspondant à l'apparition du ferromagnétisme est  $x_c = 0,37 \pm 0,01$  tandis que la concentration critique correspondant à la transition métal-non métal est  $x'_c = 0,47 \pm 0,01$ . Les résultats obtenus s'expliquent par des mécanismes de percolation de sites et de liaisons dans les systèmes désordonnés. Les propriétés de  $\text{Ni}(\text{As}_x\text{S}_{1-x})_2$  sont brièvement décrites.

**Abstract.** — The magnetic and electrical properties of  $\text{Co}(\text{As}_x\text{S}_{1-x})_2$  are investigated and the phase diagrams are shown. In  $\text{Co}(\text{As}_x\text{S}_{1-x})_2$ , the outbreak concentration of the ferromagnetism is obtained to be  $x_c = 0.37 \pm 0.01$ , while the critical concentration of the metal-non metal transition is determined to be  $x'_c = 0.47 \pm 0.01$ . The results obtained are explained by site and bond percolation mechanisms in the disordered system. The properties of  $\text{Ni}(\text{As}_x\text{S}_{1-x})_2$  are mentioned briefly.

**1. Introduction.** — The investigation of magnetic and electrical properties of pyrite type compounds offers interesting problems on the mechanism of occurrence of magnetism and on the origin of metal-non metal transition [1, 2, 3, 4]. Especially, the investigations for the solid solution between these compounds relate to the following subjects for the disordered system : (1) The metal-non metal (M-NM) transition and the critical concentration for a percolation conduction, (2) the magnetic phase diagram of a disordered interacting system and the outbreak concentration of a magnetic order and (3) the constitution of narrow  $d(e_g$  and  $t_{2g})$  band under given electron numbers in the solution.

In this paper, with the purposes mentioned above, the two kinds of solid solution,  $\text{Co}(\text{As}_x\text{S}_{1-x})_2$  and  $\text{Ni}(\text{As}_x\text{S}_{1-x})_2$  with pyrite structure for  $0 \leq x \leq 0.5$ , are investigated. Here, the outlines of the magnetic and electrical properties and the crystal structure for the both sides compounds ( $x = 0$  and  $x = 0.5$ ) are given as follows.  $\text{CoS}_2$  is a ferromagnetic substance [5] with a metallic conduction [1],  $\text{CoAsS}$  is a weakly-constant paramagnetic substance and the conduction is semiconductive [1], where the electronic structure can be regarded as  $\text{Co}^{3+}\text{As}^{2-}\text{S}^-$  and  $\text{Co}^{3+}$  has  $t_{2g}^6e_g^0$  electron configuration in low spin state as similar to that of  $\text{FeS}_2$ . Therefore, the plausible ionic configuration of  $\text{Co}(\text{As}_x\text{S}_{1-x})_2$  can be expressed as



with  $0 \mu_B$  of  $\text{Co}^{3+}$  and  $1 \mu_B$  of  $\text{Co}^{2+}$  ion. On the other hand,  $\text{NiS}_2$  [2, 6, 7] is an antiferromagnetic substance with a weak ferromagnetism and the conduction is

semiconductive, which is regarded as a Hubbard gap antiferromagnet. While,  $\text{NiAsS}$  shows a metallic conduction, however the magnetic properties are not known yet. Though the electronic structure of  $\text{NiAsS}$  can be expressed by  $t_{2g}^6e_g^1$  from the similar consideration to  $\text{CoAsS}$ , the simple ionic electron configuration is inadequate as shown below. As for the crystal structure [8], the space group of  $\text{CoS}_2$ ,  $\text{CoAsS}$  and  $\text{NiS}_2$  is  $T_h^6\text{-Pa}3$ , so called pyrite structure, while  $\text{NiAsS}$  [9] is  $T^4\text{-P}2_13$  due to an ordering of As and S atoms with a small distortion of Ni atom from the pyrite structure.

The magnetic and electrical properties of  $\text{Co}(\text{As}_x\text{S}_{1-x})_2$  are mainly presented in this paper, while the results of  $\text{Ni}(\text{As}_x\text{S}_{1-x})_2$  are shown briefly, the details for the latter will be presented elsewhere.

**2. Experimentals.** — 2.1 SAMPLE PREPARATION. — The powdered samples were synthesized at 800 to 850 °C for  $\text{Co}(\text{As}_x\text{S}_{1-x})_2$  and at 700 to 750 °C for  $\text{Ni}(\text{As}_x\text{S}_{1-x})_2$  by a usual sintering method [2, 9]. The pyrite and the related structure were confirmed by X-ray analysis and a nearly linear dependence of the lattice constant on  $x$ , giving  $a = 5.534 \text{ \AA}$  and  $a = 5.579 \text{ \AA}$  for  $\text{CoS}_2$  and  $\text{CoAsS}$  :  $a = 5.692 \text{ \AA}$  and  $a = 5.687 \text{ \AA}$  for  $\text{NiS}_2$  and  $\text{NiAsS}$ , was obtained. For  $\text{Ni}(\text{As}_x\text{S}_{1-x})_2$ , the boundary of structures of  $T_h^6$  to  $T^4$  is obtained to be  $x \simeq 0.35$ .

2.2 MAGNETIC PROPERTIES OF  $\text{Co}(\text{As}_x\text{S}_{1-x})_2$ . — The magnetization curve, the thermomagnetic behaviour and the magnetic susceptibility were measured from 4.2 K to 600 K under magnetic field strength up to 17 kOe. A part of the magnetic investigation has been done by reference [9].

The magnetic susceptibility is shown in figures 1a and 1b. The inverse susceptibilities for  $0.10 < x \leq 0.3$  are slightly concave to the temperature axis (Fig. 1a). The effective moment and the paramagnetic Curie

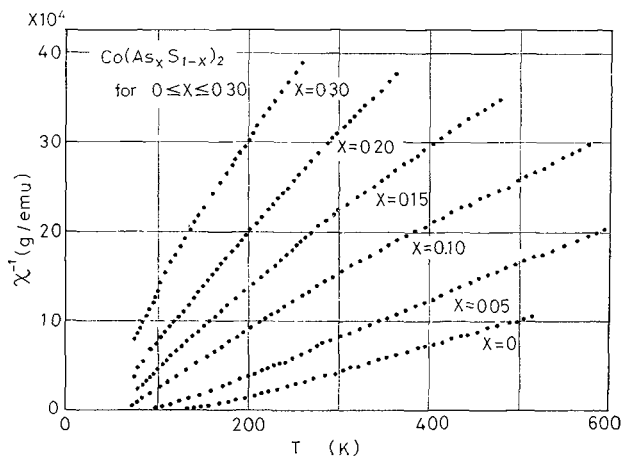


FIG. 1a. — The inverse magnetic susceptibility vs. temperature of  $\text{Co}(\text{As}_x\text{S}_{1-x})_2$  for  $0 \leq x \leq 0.30$ , ( $\chi^{-1}(T)$ ).

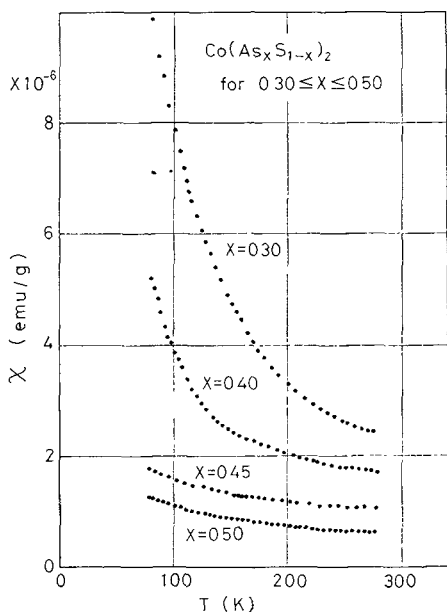


FIG. 1b. — The magnetic susceptibility vs. temperature of  $\text{Co}(\text{As}_x\text{S}_{1-x})_2$  for  $0.30 \leq x \leq 0.50$ , ( $\chi(T)$ ).

point,  $p_{\text{eff}}$  and  $\theta_p$  respectively, can be estimated by the susceptibility. While, for  $0.3 < x \leq 0.5$ , the  $\chi^{-1}(T)$  curve does not follow a Curie-Weiss law and the susceptibility tends towards weak paramagnetism at  $x = 0.5$ .

On the other hand, the magnetization and the thermomagnetic curves, the Curie point ( $T_c$ ) and the critical concentration ( $x_c$ ) for the outbreak of the ferromagnetism were determined by an asymptotic law of saturation and by Arrott plot method. The atomic moments at 0 K per Co and  $\text{Co}^{2+}$  ion are shown in

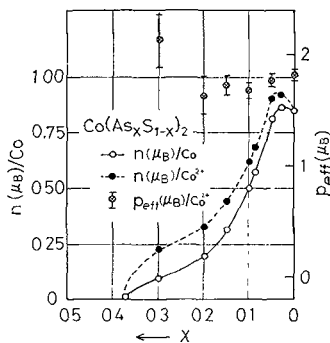


FIG. 2. — The atomic magnetic moments of  $\text{Co}(\text{As}_x\text{S}_{1-x})_2$  per Co atom (solid curve) and per  $\text{Co}^{2+}$  ion (broken curve) respectively, and the effective moment per  $\text{Co}^{2+}$  ion obtained from  $\chi^{-1}(T)$  curve.

figure 2 with the values of  $p_{\text{eff}}$  per  $\text{Co}^{2+}$  ion. The atomic moment first increases then decreases abruptly and gradually with increasing  $x$  towards

$$x_c = 0.37 \pm 0.01.$$

The variations of  $T_c$  and  $\theta_p$  are shown in figure 3 with the boundary of the M-NM transition indicated

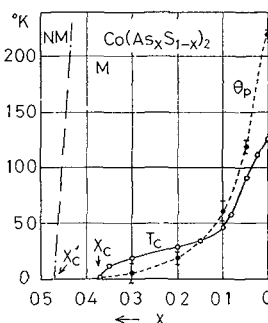


FIG. 3. — The Curie ( $T_c$ ) and the paramagnetic Curie ( $\theta_p$ ) points of  $\text{Co}(\text{As}_x\text{S}_{1-x})_2$ , the boundary between the metal and non metal regions denoted by M and NM.

below. The  $T_c$  and  $\theta_p$  decrease rapidly up to  $x = 0.1$  then gradually to  $x_c$  with increasing  $x$ . The evidence of  $\theta_p < T_c$  in the  $\chi^{-1}(T)$  curves for  $0.15 < x < x_c$  implies an introduction of certain weakly antiferromagnetic superexchange interaction for the bond  $\text{Co}^{2+}\text{-As-Co}^{2+}$  by the As-substitution.

2.3 ELECTRICAL RESISTIVITY OF  $\text{Co}(\text{As}_x\text{S}_{1-x})_2$ . — The electrical resistivity was measured by 4-terminal method in the range of temperature 4.2 K to 570 K. The variation of the resistivity are shown in figures 4a, 4b and 4c. In  $\text{CoS}_2$  ( $x = 0$ ), a hump in the resistivity [10] appears just below  $T_c$  ( $T_c$  is marked by an arrow). When  $x$  increases, the hump seems to be exaggerated, then it disappears at  $x = 0.15$ . As shown in figure 4b, the M-NM transition occurs at the concentration of  $x'_c$ ,

$$0.45 < x'_c < 0.48.$$

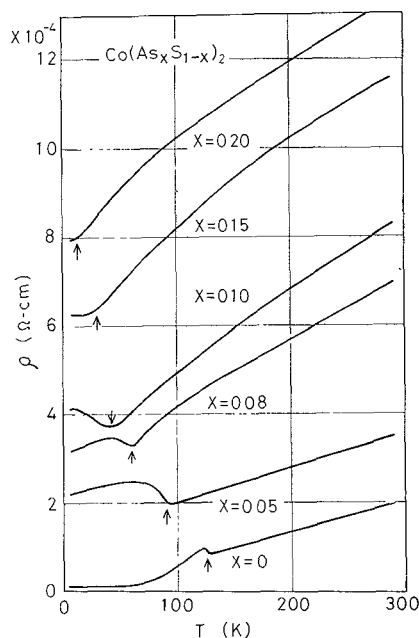


FIG. 4a. — The electrical resistivity of  $\text{Co}(\text{As}_x\text{S}_{1-x})_2$  for  $0 \leq x \leq 0.20$ . The arrow indicated in the figure is the Curie point.

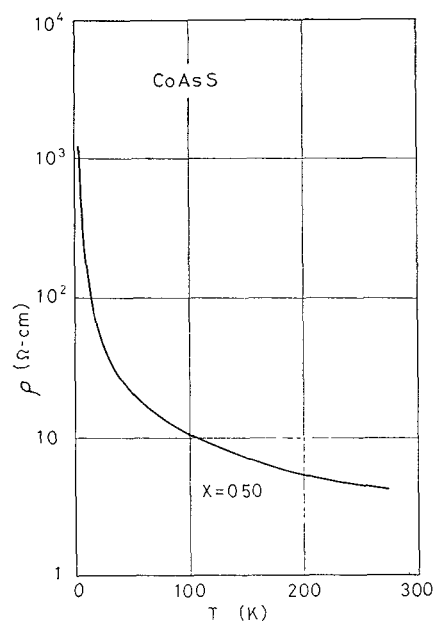


FIG. 4c. — The electrical resistivity of  $\text{CoAsS}$  ( $x = 0.50$ ).

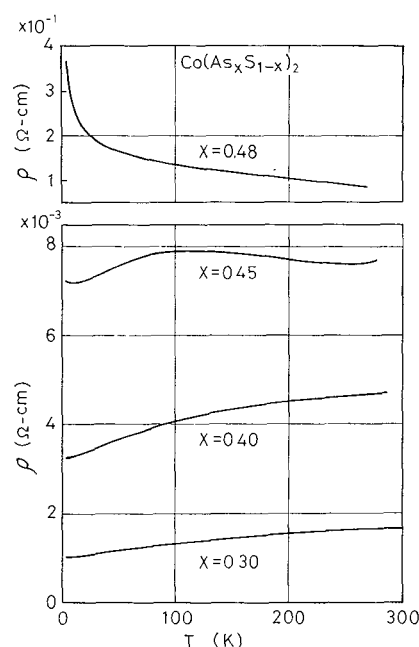


FIG. 4b. — The electrical resistivity of  $\text{Co}(\text{As}_x\text{S}_{1-x})_2$  for  $0.30 \leq x \leq 0.48$ .

The value of  $x'_c$  can be estimated as  $x'_c = 0.47 \pm 0.01$ . The boundary of M-NM transition is shown in figure 3.

Thus, the critical concentration of the M-NM transition ( $x'_c$ ) gives the larger value than that of the magnetic one ( $x_c$ ). This evidence suggests some different mechanisms for the critical percolations on the electron current and on the spin ordering in the disordered lattice.

The value of resistivity for  $x > 0.45$  increases rapidly with increasing  $x$ . The  $\rho(T)$  curves for  $x \geq 0.48$  show a semiconductive behaviour, and the activation energy in the temperature range of  $T > 250$  K is estimated to be  $E_g = 0.18$  eV and  $E_g = 0.60$  eV for  $x = 0.48$  and  $x = 0.50$  respectively, where

$$\rho(T) \propto \exp(E_g/2kT)$$

is used. The results can be interpreted on the basis of the band theory as follows. In  $\text{CoAsS}$ , the energy gap between  $t_{2g}$  (valence band) and  $e_g$  (conduction band) is given to be 0.60 eV, while when a small amount of S atoms is substituted by As atoms in  $\text{CoAsS}$ , excess electrons does not enter directly into the  $e_g$ -band but they form an impurity level as a donor locating at 0.18 eV below the  $e_g$ -band.

**2.4 MAGNETIC AND ELECTRICAL PROPERTIES OF  $\text{Ni}(\text{As}_x\text{S}_{1-x})_2$ .** — In this section, the magnetic and electrical properties of  $\text{Ni}(\text{As}_x\text{S}_{1-x})_2$  are presented briefly. The phase diagram is shown in figure 5. The electrical resistivity at  $x = 0.10$  shows a resistance minimum at 50 K, where this point is defined as the boundary between M-NM states. Thus, the critical M-NM concentration at 0 K is determined to be  $x'_c = 0.12 \pm 0.01$ . The behaviour can be interpreted as the disappearance of Hubbard gap due to the decrease of  $e_g$  electrons with increasing  $x$ , and  $x'_c = 0.12$  corresponds to  $e_g^{1.76}$ , when  $e_g^2$  for  $\text{NiS}_2$  and  $e_g^1$  for  $\text{NiAsS}$  are assumed.

As for the magnetic state, the Néel point in the non-metallic region increases rapidly with increasing  $x$  and the  $T_N$  connects to the metallic state. However,

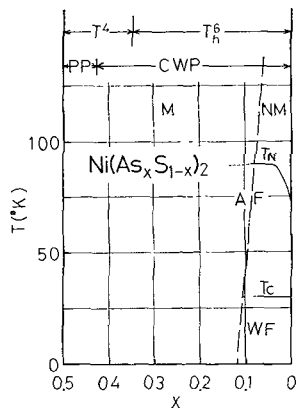


FIG. 5. — The magnetic phase diagram of  $\text{Ni}(\text{As}_x\text{S}_{1-x})_2$ .  $T_N$  and  $T_c$  are the antiferromagnetic (AF) and the weakly ferromagnetic (WF) transition points respectively. CWP and PP are the Curie-Weiss' and Pauli's paramagnetisms for the susceptibility respectively. The boundary between metal (M) and nonmetal (NM) phases are shown in the chained curve.

the curve of  $T_N(x)$  and the critical point ( $x_c$ ) cannot be determined by our susceptibility and resistivity measurements, because the anomaly at  $T_N$  vanishes gradually with increasing  $x$ . On the other hand, the Curie point of the weak ferromagnetism can be observed in the range of  $0 \leq x < 0.10$ , and  $T_c$  does not change in this region, while the moment of the weak ferromagnetism at 0 K diminishes suddenly with  $x$  and vanishes at  $x_c = 0.10$ .

In the M-region of  $x < 0.43$ , the magnetic susceptibility behaves as a Curie Weiss type with negative  $\theta_p$ , in  $x > 0.43$ , however, it changes to a Pauli's paramagnetism with the magnitude of  $\chi_p \approx 10^{-7}$  emu/g and  $d\chi_p/dT < 0$ . Therefore, the electronic structure of  $\text{NiAsS}$  is different to that of  $\text{CoS}_2$  (ferromagnetic). In addition to this, since the crystal structure changes from  $T_h^6$  to  $T_h^4$  at  $x \approx 0.35$ , it is considered that the simple ionic configuration should not be applied to the electron state of  $\text{NiAsS}$ .

**3. Discussions on  $\text{Co}(\text{As}_x\text{S}_{1-x})_2$ .** — In this paragraph, some statistical-mechanical discussions on the magnetic as well as the electric properties of  $\text{Co}(\text{As}_x\text{S}_{1-x})_2$  are given. Here, the disordered system  $\text{Co}(\text{As}_x\text{S}_{1-x})_2$  is regarded as a localized spin system being possible to have site and bond percolations rather than the band scheme.

So far as the magnetic disordered state written by  $\text{Co}_{2x}^{3+}\text{Co}_{1-2x}^{2+}(\text{As}_x^{2-}\text{S}_{1-x}^{2-})_2$  is concerned, there exist two kinds of simultaneous disorder, that is the site disorder of  $\text{Co}^{3+}$  ( $0 \mu_B$ ) and  $\text{Co}^{2+}$  ( $1 \mu_B$ ) and the bond disorder indicated by  $\text{Co}^{2+}\text{-S}\text{-Co}^{2+}$  and  $\text{Co}^{2+}\text{-As}^{2-}\text{-Co}^{2+}$  with ferro- and antiferromagnetic interactions. The site percolation probability due to the production of  $\text{Co}^{2+}$  ions in the random lattice can be written by  $p_s = 1 - 2x$ , while the bond percolation

one is also defined as  $p_b = 1 - 2x$  by the origin of the band structure mentioned in 2 in which no percolation bond at  $x = 0.5$  corresponds to the full  $t_{2g}$  band. The change of Curie point with the  $p$  value due to the paramagnetic dilution in a ferromagnet of Heisenberg type has been given theoretically in the cases of the site- and the bond-disordered systems in fcc lattice [11];  $t_c(p_s) = T_c(p_s)/T_c(1)$  and  $t_c(p_b) = T_c(p_b)/T_c(1)$  respectively, where the critical value is given to be  $p_{sc} = 0.195$  and  $p_{bc} = 0.119$  respectively. In the case of  $\text{Co}(\text{As}_x\text{S}_{1-x})_2$ , the  $t_c$  can approximately be given by  $t_c = t_c(p_s) \cdot t_c(p_b)$  due to the multiple effect, and the critical  $p$  value is controlled by  $p_{sc}$ . As shown in figure 6,

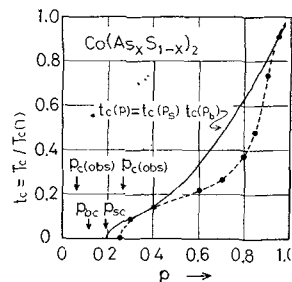


FIG. 6. — The observed (black circle) and the calculated (solid curve) Curie point ( $t_c$ ) of  $\text{Co}(\text{As}_x\text{S}_{1-x})_2$  vs. percolation probability ( $p$ ).  $p_c$  and  $p'_c$  are the critical values for the outbreak point of ferromagnetism and the metal-non metal transition point respectively.  $t_c(p_s)$  and  $t_c(p_b)$  are the  $t_c$  due to site and bond percolations in fcc lattice respectively.

the theoretical result shows a similar tendency to the observed one. Some depression of the observed value as compared with the theoretical one is considered to be due to the effect of the antiferromagnetic superexchange interaction via  $\text{Co}^{2+}\text{-As}^{2-}\text{-Co}^{2+}$  as explained above. The theoretical result gives  $p_c = p_{sc} = 0.195$ , however the experimental one is  $p_c = 0.26 \pm 0.2$ . The value of  $p_c$  may be affected by the antiferromagnetic interaction.

On the other hand, in the electric conduction phenomena, the bond percolation has an important role. Then, the critical  $p$  value is determined to be  $p_{bc} = p'_c = 0.119$  in the theory. However the observed value is given to be  $p'_c = 0.06 \pm 0.02$ . Thus, the difference of  $p_c - p'_c$  in the experiment is larger than that in the theory, as shown in figure 6. While, the small value of  $p_c \approx 0.06$  can occur by another origin such as a metallic conduction in the impurity band located below the  $e_g$ -band for  $x = 0.45$ .

In conclusion, it is noted that the values of  $p_c$  and  $p'_c$  are influenced by some clustering or ordering type atomic arrangement in the disordered state. Therefore in order to discuss in details, it is necessary to take this effect into account. In addition to this, it cannot neglect the effects of the band structure and the electron state in the disordered state for the real substance.

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