Study of Semiconductor-to-Metal Transition in Mn-Doped $FeSi_2$

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The electrical resistivity, the thermoelectric power, and the Hall coefficient for $FeSi_2$ doped with Mn or Co have been measured over the temperature range 300–1400 K. The energy gaps deduced from the slopes of curves of the resistivity versus reciprocal absolute temperature decrease with increasing Mn concentration. The resistivities and thermoelectric powers show a semiconductor-to-metal transition with hysteresis, and the transition temperature decreases with increasing Mn concentration. Specimens both doped with Mn and undoped are found to be p-type semiconductors in the temperature range below the transition temperature. The added Mn acts as an acceptor. The analysis of resistivity in the semiconducting state was based on a model predicting that the narrow band in the metallic state is split by the crystalline-structure distortion. The density of states for the undoped specimen is found to be 7.46×10^{22} cm^{-3}. Assuming that the value of the density of states is invariable in all specimens, the analyzed results are in reasonable agreement with the resistivities observed in the intrinsic region.

I. INTRODUCTION

The compound $FeSi_2$ changes from a metallic high-temperature phase to a semiconducting low-temperature phase at 1259 K.[1] The metallic phase deviates from the stoichiometric composition. It has a tetragonal structure with about 13% Fe vacancies.[2] It is an alloy consisting of a tetragonal structure with 2.87 atoms in a unit cell[3] and a cubic structure with eight atoms in a unit cell.[4] On the other hand, the semiconducting phase has a stoichiometric composition and presents an orthorhombic structure with 48 atoms in a unit cell.[5] Although the atomic positions in the structure are not yet exactly known, the structure probably changes to tetragonal symmetry at the transition temperature.[6,7]

The thermoelectric properties for $FeSi_2$ doped with Al (p-type) or Co (n-type) have been reported by several investigators in relation to thermoelectric conversion.[2,8–10] The conduction mechanism was investigated by Birkholz and Schelm[11] and Hesse,[12] showing that the conduction in p- and n-type $FeSi_2$ could be interpreted using the band and polaron models, respectively. A few investigations concerning the semiconductor-to-metal transition were made to explain the mechanisms of the electrical resistivity[7] and of the magnetic susceptibility[13] for n-type $FeSi_2$. However, the measurement of the detailed Hall coefficient and the study of the transition mechanism have not been carried out on p-type $FeSi_2$.

In the present study it was found that the electrical properties of $FeSi_2$ are modified by Mn doping, resulting in a considerable increase of the hole concentration and decrease of the energy gap. In order to clarify the transition mechanism of $FeSi_2$ doped with Mn, measurements of resistivity, thermoelectric power, and Hall coefficient have been made over the temperature range 300–1400 K.

II. EXPERIMENTAL

The compounds of $FeSi_2$ were prepared by melting the stoichiometric amounts of zone-refined iron (99.997 wt% pure) and n-type silicon single crystal (99.998 wt% pure) in an argon atmosphere. Compounds of $FeSi_2$ doped with Mn or Co were also obtained by remelting $FeSi_2$ with $MnSi_2$ or $CoSi_2$ in a helium atmosphere. They were then ground into a fine powder of a few microns in size, and hot-pressed into blocks 6 mm^2 by 30 mm in an argon atmosphere at 1150 °C for 8 min under a pressure of about 300 kg/cm^2. The blocks were annealed in an evacuated quartz tube at 800 °C for 100 h. They were shown to be single phase by x-ray analysis. In order to measure the electrical resistivity, thermoelectric power, and Hall coefficient, the specimens were cut into plates of about $0.1\times4\times15$ mm using a diamond wheel. The thermoelectric properties were measured in a helium atmosphere at 100 Torr in the temperature range 300–1400 K, using the same method as reported by Sakata and Tokushima.[14]

III. RESULTS AND DISCUSSION

The temperature dependence of the resistivity, thermoelectric power, and Hall mobility is shown in Figs. 1, 2, and 3, respectively, as functions of absolute temperature. As shown in Fig. 1, all specimens have a semiconductor-to-metal transition with hysteresis and the jump of resistivity ρ is about one order of magnitude. Both transition temperature T_c and the slope of ρ in the intrinsic region decrease with increasing Mn concentration x. The values of T_c and energy gap E_g deduced from the slopes of ρ vs T^{-1} are tabulated in Table I. The specimens quenched from a temperature of 1100 °C are in a metastable phase with metallic

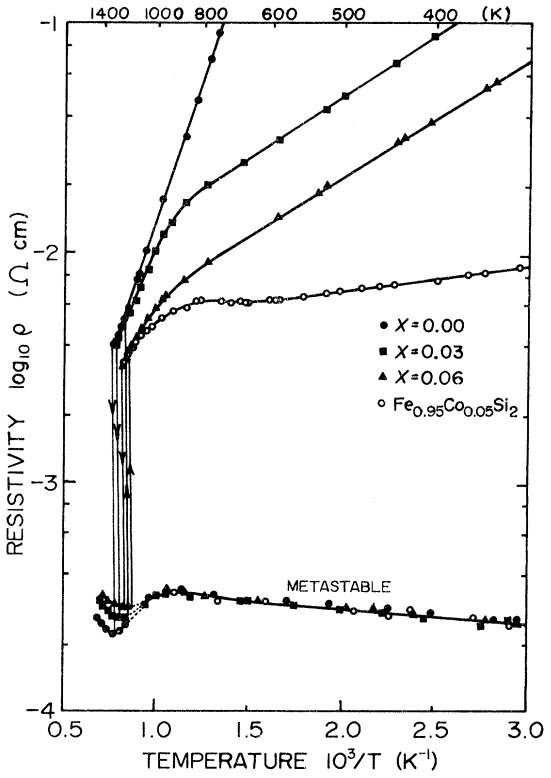

FIG. 1. Temperature dependence of resistivity for p-type $Fe_{1-x}Mn_xSi_2$. Both the heating and cooling transition directions are indicated by arrows, and the open circle is n-type $FeSi_2$.

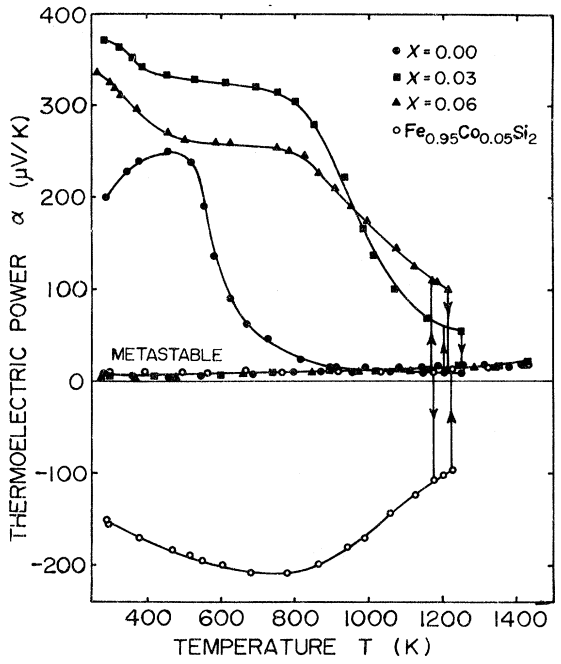

FIG. 2. Temperature dependence of thermoelectric power for p-type $Fe_{1-x}Mn_xSi_2$. Both the heating and cooling transition directions are indicated by arrows, and the open circle is p-type $FeSi_2$.

conduction; also the changes in ρ are found to be independent of x in the temperature range below 900 K.

The Hall coefficient R and thermoelectric power α measurements show that the signs of the semiconducting specimens doped with Mn or Co are positive or negative, respectively, in the temperature range below T_c. The hole concentrations in $Fe_{1-x}Mn_xSi_2$ are 2.85×10^{17} cm^{-3} for $x=0.00$, 2.72×10^{18} cm^{-3} for $x=0.03$, and 5.08×10^{18} cm^{-3} for $x=0.06$ at room temperature. The electron concentration in $Fe_{0.95}Co_{0.05}Si_2$ is 1.9×10^{21} cm^{-3} at room temperature. Therefore, it was found that the Mn or Co atoms act as acceptors or donors, respectively. The temperature dependence of α for semiconducting $Fe_{1-x}Mn_xSi_2$ and $Fe_{0.95}Co_{0.05}Si_2$ in Fig. 2 is similar to curves in Figs. 5 and 6 of Birkholz and Schelm,[11] respectively. The transition temperature of α is in good agreement with that of the resistivity. On the other hand, the specimens with metallic properties are whole p-type conductors and the values of α are 6–12 μV/K in this experiment. In the temperature range above T_c the Hall coefficient is very small and of the order of 10^{-5} cm^3/C. As shown in Fig. 3, the Hall mobility $\mu_H = R/\rho$ shows the temperature dependence for p type and is independent of temperature for n-type specimens in the extrinsic temperature region 300–600 K. The values for hole and electron mobility are 7.5 and 0.35 cm^2/V sec at 300 K. This suggests that the ratio of electron to hole mobility b has large temperature dependence and that the narrow bands contributed to the conduction.

An analysis of ρ in the semiconducting state was based on a model that the narrow band in the metallic state is split by the crystalline-structure distortion, as in V_2O_3, VO_2, and NbO_2.[15,16] This model, in which the change in E_g is represented by the relationship between carrier concentration and Jahn–Teller effect, has been developed by Adler

TABLE I. Energy gaps determined experimentally and parameters at semiconductor-to-metal transition temperature used in the analysis of resistivities for $Fe_{1-x}Mn_xSi_2$. T_c shows transition temperatures in the heating process which are higher than those in the cooling one.

x	T_c (K)	E_g (eV)	b	$\bar{\delta}$	E_{g0} (eV)
0.00	1260	0.95	0.33	0.386	0.940
0.03	1253	0.92	0.32	0.371	0.926
0.06	1218	0.80	0.30	0.339	0.814

and Brooks.[17] From the narrow-band approximation in the model, the change in E_g is expressed by

$$E_g = E_{g0}\,(1 - n_i/(1-\bar{\delta})N)\,, \qquad (1)$$

where $\bar{\delta} = \delta + D(1-\delta)/E_{g0}$, E_{g0} is the zero-temperature gap, n_i is the carrier concentration, N is the density of state, δ is the deviation of splitting from the symmetric case, and D is a factor which is small and positive. At the transition temperature T_c, the ratios E_{g0}/kT_c (where k is Boltzmann's constant) and n_i/N are given by a function of $\bar{\delta}$. Therefore, the resistivity of the semiconducting phase in the intrinsic region is expressed by

$$\rho = \rho_0 \exp\,(1 - n_i/(1-\bar{\delta})N)\,(E_{g0}/2kT)\,, \qquad (2)$$

where ρ_0 is the resistivity, which is independent of temperature. Furthermore, the carrier concentration for p-type semiconductor in the intrinsic region is represented by

$$n_i = (1/e\rho\mu_p + n_s\, b)/(1+b)\,, \qquad (3)$$

where μ_p is hole mobility and n_s is the saturated carrier concentration.[18] The ratios of electron to hole mobility at T_c were determined by extrapolating μ_H in the extrinsic region up to T_c, and those values are also tabulated in Table I.

The value of n_i for undoped $FeSi_2$ at T_c was found to be 1.12×10^{21} cm^{-3} using Eq. (3). From both values of n_i and $E_g = 0.95$ eV determined experimentally for undoped $FeSi_2$, a value of $\bar{\delta}$ was estimated to be 0.015, and also a value of N was determined to be 7.46×10^{22} cm^{-3} from the relationship between $\bar{\delta}$ and n_i/N.[17] Assuming that the value of N is invariable on all specimens, the values of $\bar{\delta}$ and E_{g0} were evaluated from n_i at various T_c and those results are also tabulated in Table I. The values of E_{g0} decrease with increasing x and are in good agreement with that observed. Substituting the values of E_{g0}, $\bar{\delta}$, and T_c into Eq. (2), in the temperature range below T_c, the resistivities were calculated and shown in Fig. 4 as solid curves. Both values of $\rho_0 = 4.0\times10^{-5}$ Ω cm determined experimentally and n_i calculated using Eq. (3) at various temperatures were used for the calculation. The results, shown in Fig. 4, are in reasonable agreement with the observed resistivities in the intrinsic region. Therefore the resistivity and transition temperature for the p-type $FeSi_2$ is explained by a narrow-band approximation associated with the crystalline-structure distortion.

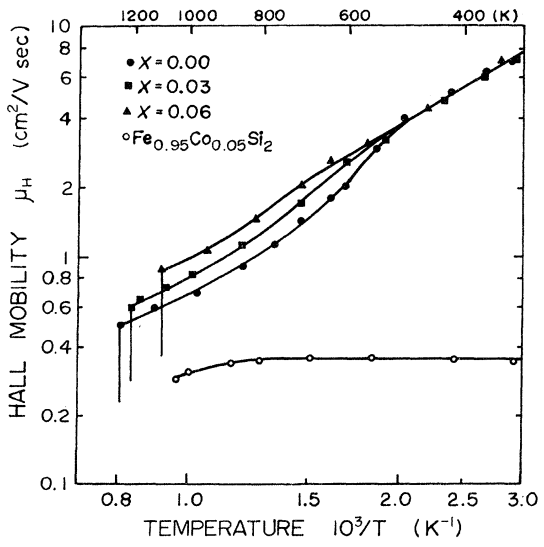

FIG. 3. Temperature dependence of Hall mobility for p-type $Fe_{1-x}Mn_xSi_2$. The open circle is n-type $FeSi_2$.

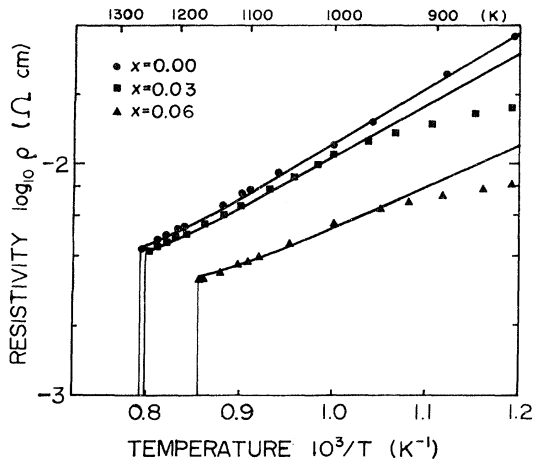

FIG. 4. Temperature dependence of resistivity for p-type $Fe_{1-x}Mn_xSi_2$ in the intrinsic region. The solid curves represent the calculated value.

IV. SUMMARY

The thermoelectric properties of $FeSi_2$ were modified by doping with Mn, resulting in a considerable increase of the hole concentration and decrease of the energy gap. The hole concentration in $Fe_{1-x}Mn_xSi_2$ is 2.85×10^{17} cm^{-3} for $x = 0.00$, 2.72×10^{18} cm^{-3} for $x = 0.03$, and 5.08×10^{18} cm^{-3} for $x = 0.06$ at room temperature. Both the energy gap and the semiconductor-to-metal transition temperature decrease with increasing Mn concentration. The analysis of resistivity in the intrinsic region was based on a model that the narrow band is split by the crystalline distortion at the transition temperature. The results indicate that the density of state for $FeSi_2$ is 7.46×10^{22} cm^{-3} and that the calculated resistivities for $Fe_{1-x}Mn_xSi_2$ are in reasonable agreement with the observed values in the intrinsic region.

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Brillouin-Scattering Studies of Acoustoelectric Gain and Lattice Attenuation in Semiconducting CdS

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Brillouin-scattering measurements were used to study acoustoelectric interactions in semiconducting CdS. In the GHz frequency range, a double-pulse technique described earlier was employed to suppress domain formation and thereby reduce down-conversion processes. In this manner considerable extension of the small-signal regime towards higher flux levels could be achieved. At lower frequencies, nonlinear effects were invoked to produce a propagating low-frequency domain whose attenuation and amplification were subsequently studied under small-signal conditions. Analysis of the time evolution of the spatial and frequency distribution of the amplified flux, measured under different conditions, provided accurate data on the frequency dependence of the acoustoelectric gain and the lattice attenuation over the broad range of 0.15–4 GHz. Comparison of the measured gain parameters with the small-signal theory of acoustoelectric amplification gave very good agreement throughout the frequency range studied. The lattice attenuation was found to follow the expected f^2 Akhiezer law at high frequencies and to vary much more slowly, if at all, in the low-frequency range (0.2–0.6 GHz). In this latter range the lattice attenuation is very low (~ 1 cm^{-1}) and is most probably controlled by crystal imperfections. Although the studies in this paper were mostly confined to the small-signal regime, several interesting features have emerged concerning nonlinear effects. In particular, the down-converted low-frequency flux in a propagating domain was observed to lag slightly behind the high-frequency flux from which it originated. No explanation can be offered at present for this rather surprising phenomenon.

INTRODUCTION

Acoustoelectric amplification or attenuation in piezoelectric semiconductors arises from the interaction between the rather strong ac field associated with piezoelectrically active acoustic waves and the electrons (or holes) present in the crystal.[1–4] Amplification occurs when the drift velocity imparted to the electrons by an external dc field exceeds the sound velocity. Such amplification is selective in both frequency and direction of propagation. Only phonons within a bandwidth centered around some optimal frequency and propagating in a narrow cone around the direction of electron drift are amplified. Under small-signal conditions the optimal frequency is determined by the material parameters. At larger acoustic intensities, there is usually a progressive shift in the spectrum towards lower frequencies resulting from nonlinear down-conversion pro-