Temperature dependence of the magnetic susceptibility of a $CrSi_2$ single crystal

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A single crystal of $CrSi_2$ was grown by a modified floating-zone refining technique, and its magnetic susceptibilities and Hall coefficients in the directions of both the a and c axes were measured over a temperature range from room temperature to 1000 K. The susceptibilities were constantly negative over the temperature range and possessed a minimum value at 770 K. The temperature dependence of the hole concentration estimated from observed data of the Hall measurement suggested that above 770 K the susceptibility is primarily dominated by the contribution from charge carriers. The chemical composition of the crystal was estimated at $CrSi_{1.985}$ by quantitative chemical analysis. A theoretical curve of susceptibility was calculated by assuming that the excess Cr atoms act as Cr^{3+} ions in the crystal. The observed susceptibilities were in good agreement with the theoretical curve. It was concluded that the Cr atoms constituting a stoichiometric $CrSi_2$ lattice are quadrivalent by reason of their negligibly small contribution to the susceptibility.

I. INTRODUCTION

Many investigations have been made on the thermoelectricity of transition-metal silicides to investigate the semiconducting properties of $CrSi_2$,[1-5] $MnSi_2$,[6-8] and β-$FeSi_2$.[9-12] These silicides are of interest in application to thermoelectric generators in a high-temperature atmosphere because of their high melting points, comparatively low resistivities, and high thermoelectric powers.[13] The crystal structure of $CrSi_2$ is classified in the space group D_{6h}^4 with lattice constants of $a=4.422\pm0.005$ Å and $c=6.351\pm0.005$ Å, of which ratio c/a equals 1.44.[14] Anisotropic resistivity and thermoelectric power have been observed in $CrSi_2$, and they have quantitatively been analyzed to evaluate the anisotropic effective mass of holes in a $CrSi_2$ single crystal.[15] Several reports have also been published to indicate the unusual diamagnetism of $CrSi_2$, but its details have not been clarified yet.[16-18] The temperature dependence of the magnetic susceptibility is known to reach a minimum at a certain temperature, while no identical observation has been made on the value of the minimum and its corresponding temperature.

In this experiment a single crystal of $CrSi_2$ was grown by a modified zone refining technique,[15] and the temperature dependence of magnetic susceptibilities was measured in the direction [0001] parallel to the c axis and its perpendicular direction [10$\bar{1}$0] to investigate the magnetism of this compound and the valency of the Cr atoms constituting a stoichiometric $CrSi_2$ lattice.

II. REFINING OF CrSi AND CRYSTAL GROWTH OF $CrSi_2$

The starting material consisted of 99.93% pure Cr powder, 99.99% pure Si powder, and an n-type Si single crystal with a resistivity of about 100 Ω cm at room temperature. The powders of Cr and Si weighted in a chemical composition ratio of 1:1 were well mixed and encapsulated into a quartz tube. Then the mixture was synthesized into CrSi by a solid-state reaction at 1270 K for 24 h. The CrSi obtained was ground into a fine powder of a few micrometers by using an agate mortar. The powder was hot pressed into a dimension of 6 $mm^2\times80$ mm at 1470 K for 8 min under a pressure of about 250 kg/cm^2. To obtain high-purity silicide, the sintered CrSi was refined by repeating a few repetitions of zone refining in an argon atmosphere containing 10% hydrogen at a refining rate of 3 mm/min and a rotation speed of 40 rpm with a zone temperature of 1870 K. The square specimen completely changed into a rod consisting of many tiny crystals with an average size of 9 mm. An individual crystal in the coarse-grained rod was ground into powder and identified to be in the cubic system T_1^4 with a lattice constant of $a=4.607\pm0.004$ Å by the x-ray diffraction technique. Qualitative analysis with an x-ray microanalyzer confirmed no segregation of Si and no chemical element other than Cr or Si in the crystal.

The CrSi crystal and a Si single crystal were weighted in a chemical composition ratio of 1:1 and then arc melted in an argon atmosphere. The $CrSi_2$ compound ob-

tained was so brittle to be readily broken into granular particles with a dimension of about 5 mm. The particles of $CrSi_2$ were put into a quartz tube with a conical end and a diameter of 8 mm, and then they were refined by high-frequency floating-zone refining apparatus with a carbon holder for preheating.[15] The first cycle of refining was performed at a refining rate of 0.17 mm/min and a rotation speed of 30 rpm with a zone temperature of 1870 K. The $CrSi_2$ boule grew into a dimension of about 8 mm in diameter and 35 mm in length. A portion of the boule was ground into powder and identified to be $CrSi_2$ by the x-ray diffraction technique. The boule, moreover, was confirmed to be a single crystal by Laue photography and the rotational crystal method. The results from the rotational crystal method yielded the lattice constants $a = 4.424 \pm 0.004$ Å and $c = 6.342 \pm 0.002$ Å, which were in agreement with those of polycrystalline specimens already published.[19] The growing direction of the crystal was confirmed to be in the direction of the c axis with a tilting angle less than 9° by Laue photography.

III. ESTIMATION OF HOLE CONCENTRATION AND MEASUREMENT OF MAGNETIC SUSCEPTIBILITY

A parallelepiped specimen with a dimension of $0.1 \times 4 \times 8$ mm^3 was cut off from the single crystal by a diamond wheel cutter and annealed in an evacuated quartz tube for 200 h at 1370 K to be homogenized. It was confirmed through chemical analysis that the contents of Cr and Si in the annealed specimen were 33.5% and 66.5%, respectively, and thus that chemical composition of the single crystal was expressed by $CrSi_{1.985}$, which suggested existence of excess Cr atoms.

Hall coefficients in both the parallel and perpendicular directions to the c axis were measured in a magnetic field of 5000 G by the dc method[20] over a temperature range from room temperature to 1000 K. In $CrSi_2$ positive holes play a role of charge carriers, and the Hall coefficient R is expressed, in terms of the hole concentration p, by[21]

$$R = \frac{1.2}{ep} , \tag{1}$$

where e is the elementary charge. Figure 1 shows the temperature dependence of the hole concentration estimated from the observed Hall coefficients through Eq. (1). As shown in the figure, the hole concentration p is independent of temperature in the region from room temperature to 720 K, which corresponds to the extrinsic region, while above that temperature it rapidly increases with rising temperature to enter the intrinsic region. The high saturation concentration suggests a large contribution of carriers to magnetic susceptibility.

Magnetic susceptibilities were measured in a magnetic field of 4000 G by the Faraday method in a temperature range from room temperature to 1000 K. The observed susceptibilities were constantly negative over the temperature range as shown in Fig. 2. This result is in agreement with Refs. 1–3 on the polarity of the susceptibilities, and with Refs. 1 and 2 on the fact that the susceptibilities possessed a minimum at 770 K (denoted by T_0 hereafter), but in disagreement with Refs. 1 and 2 on the absolute values of the susceptibilities and on the temperature corresponding to the minimum. The temperature at which susceptibility reached the minimum was approximately equal to that at which the carrier concentration began to increase and entered into the intrinsic region. This fact suggests that the magnetism from carriers is dominant in the total magnetic susceptibility above T_0.

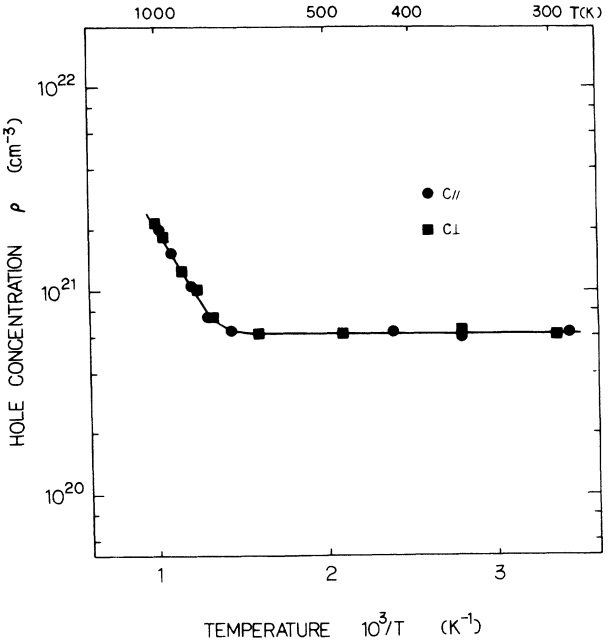

FIG. 1. Temperature dependence of the hole concentration of a $CrSi_2$ single crystal.

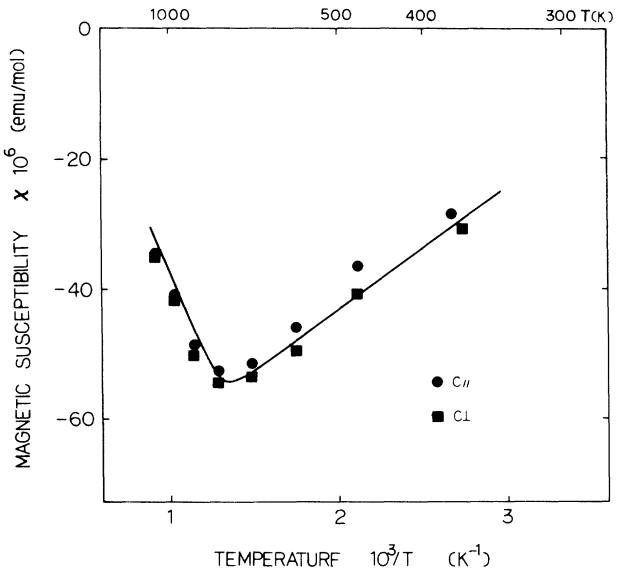

FIG. 2. Temperature dependence of the magnetic susceptibility of a $CrSi_2$ single crystal.

IV. DISCUSSION

The total susceptibility χ_{tot} may be divided into four terms, i.e., the diamagnetic susceptibility χ_d from electrons in the inner cores of Cr and Si atoms constituting a $CrSi_2$ lattice, the contribution χ_b from the outer electrons in these atoms, the contribution χ_c from the charge carriers, and the contribution χ_a from the excess Cr atoms:

$$\chi_{\text{tot}}=\chi_d+\chi_b+\chi_c+\chi_a \ . \tag{2}$$

It may be assumed that the chemical bonding in $CrSi_2$ is mainly established by four of six d electrons of a quadrivalent Cr atom, while the remaining two d electrons are localized at the Cr atom as a lone pair so that the inner core of the Cr forms an argonlike core. Assuming the inner core of Si also forms an argonlike core with a valency of -4, the contribution from the inner cores may be estimated at

$$\chi_d \simeq -58.2\times10^{-6} \ , \tag{3}$$

in emu/mol, by employing the susceptibility of Ar: $\chi_{\text{Ar}}=-19.4\times10^{-6}$ emu/mol.

The observed susceptibility was very weakly dependent on temperature in a lower region below T_0. This temperature dependence cannot be explained by assuming that Cr atoms act as Cr^{3+} or Cr^{4+} ions in the $CrSi_2$ lattice. The negligibly small contribution from Cr atoms to susceptibility may be deduced from the assumption of the ligand field that a Cr atom supplies four of its six d electrons to a Si atom to establish donor-acceptor bonding. The remaining two d electrons may be localized at the Cr atom to contribute to diamagnetism.

Magnetism from charge carriers in semiconductor is generally expressed by

$$\chi_c=\frac{w\beta^2}{3\rho kT}\left[n(3-\langle f_e^2\rangle)\frac{F'(\eta_e)}{F(\eta_e)}+p(3-\langle f_p^2\rangle)\frac{F'(\eta_p)}{F(\eta_p)}\right] , \tag{4}$$

where ρ denotes the density of specimen, k the Boltzman constant, T the absolute temperature, w the molecular weight of specimen, β the Bohr magneton, n the electron concentration, and p the hole concentration.[22,23] The factors $\langle f_e^2\rangle$ and $\langle f_p^2\rangle$ are the corrections determined from effective masses by

$$\langle f_e^2\rangle \simeq (m_0/m_e)^2 \ , \tag{5a}$$

$$\langle f_p^2\rangle \simeq (m_0/m_p)^2 \ , \tag{5b}$$

where the suffixes e and p correspond to electrons and holes, respectively, and m_0 denotes the effective mass of a free electron. The function $F(\eta)$ is the Fermi-Dirac integral defined by

$$F(\eta)=\int_0^\infty \frac{x^{1/2}}{1+\exp(x-\eta)}dx \ , \tag{6}$$

and $F'(\eta)$ is its first derivative, where η is the reduced chemical potential.[24,25] The numerical values of $F(\eta)$ and $F'(\eta)$ can precisely be calculated by series expansion or numerical integration.[26–28] The hole concentration is expressed, in terms of $F(\eta_p)$, by

$$p=\frac{4\pi(2m_pkT)^{3/2}}{h^3}F(\eta_p) \ , \tag{7}$$

and it is also related to the electron concentration n by

$$p-n=n_s \ , \tag{8}$$

where n_s denotes the saturation concentration.[21] It has been shown that the positive holes in a $CrSi_2$ single crystal possess anisotropic effective masses of $m_{p,c\parallel}=5.0m_0$ and $m_{p,c\perp}=3.0m_0$, where the subscripts $c\parallel$ or $c\perp$ denote the direction parallel or perpendicular to the c axis.[15] The mean value of the effective mass of holes m_p is consequently estimated at $(m_{p,c\parallel}m_{p,c\perp}^2)^{1/3}\simeq 3.6m_0$ by employing the values mentioned above, while m_e is assumed to be about $20.2m_0$ according to the data of polycrystalline specimens.[21] These effective masses yield very small values of the correctional factors, i.e., $\langle f_p^2\rangle<8\times10^{-2}$ and $\langle f_e^2\rangle<3\times10^{-3}$. The reduced chemical potential of electrons η_e is expressed by

$$\eta_e=-E_g/kT-\eta_p \ , \tag{9}$$

where E_g denotes the energy gap that is estimated at 0.32 eV in the case of $CrSi_2$, so that the values of η_p, η_e, and n can be calculated from the observed hole concentration by using Eqs. (7)–(9). The contribution from carriers χ_c can consequently be estimated by substituting these values into Eq. (4).

The chemical constitution of the single crystal grown in this work, namely, $CrSi_{1.985}$, suggests the existence of excess Cr atoms. Assuming that one excess Cr atom supplies one positive hole, the stoichiometric hole concentration is estimated at 3.92×10^{20} cm^{-3}, which is consistent with previous reports.[29] Consequently, we shall assume that a $CrSi_2$ lattice is constituted by quadrivalent Cr and Si, and that the excess Cr atoms are contained as Cr^{3+} ions in the crystal. The contribution from these ionic cores is estimated by

$$\chi_a=\frac{wN\beta^2}{3\rho kT}p_{\text{eff}}^2 \ , \tag{10}$$

where N denotes the number of the excess Cr atoms and p_{eff} the effective number of Bohr magnetons which is estimated at 3.87 for Cr^{3+} on the assumption of quenching of the orbital angular momentum.[30,31] The total magnetic susceptibility can theoretically be calculated by summing up the Eqs. (3), (4), and (10), where χ_b is ignored by reason of its negligibly small contribution to the total susceptibility. The theoretical curve obtained from this calculation shows a similar temperature dependence as the observed data, except for a somewhat stronger diamagnetic contribution.

It may be expected that in a $CrSi_2$ lattice each Cr atom supplies four of six d electrons for bonding with Si atoms, while the remaining two d electrons tend to localize at the Cr atom and to form a lone pair, which may enhance the diamagnetic term.[30,31] Assuming that the diamagnet-

ic term may be substituted by -83×10^{-6} emu/mol other than the value calculated from Eq. (3), we obtain the theoretical curve shown in Fig. 2 for the total susceptibility. As shown in the figure, the theoretical curve is in good agreement with the observed data, except for the small anisotropy which tends to decrease with rising temperature.

It is concluded from the above discussion that at low temperatures the total susceptibility is dominated mainly by the ionic contribution χ_a, while at high temperatures it is dominated strongly by the carrier concentration χ_c. Assuming that the angular momentum of the d electrons of Cr^{3+} ions is not completely quenched in the present case, the ionic contribution χ_a will retain some weakly anisotropic components. As the temperature rises, the anisotropic contribution χ_a decreases in inverse proportion to the temperature, while the isotropic contribution χ_c increases exponentially, so that the anisotropy of the total susceptibility may decrease and vanish in a high-temperature range above T_0.

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