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Magnetic properties of liquid Ti–Si, V–Si and Cr–Si alloys

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Abstract

The magnetic susceptibilities of liquid Ti–Si, V–Si and Cr–Si alloys have been measured as a function of composition and temperature. The magnetic susceptibilities were found to be almost independent of temperature, which suggests that transition metal solutes in liquid Si are in the non-magnetic state. The impurity susceptibilities were estimated under the assumption that the solute atoms are monovalent in liquid Si. The general trend obtained for the whole series of 3d solutes in liquid Si shows a sharp peak around Mn solute which is considerably less pronounced than that reported in liquid In or Sn. The results are discussed in terms of Anderson's model of localized impurity states.

Keywords: Magnetic susceptibility; Transition metal; Liquid Si; Impurity susceptibility; Anderson model

1. Introduction

When a transition metal (TM) solute is dissolved into liquid Si, the 3d electron states of the solute are strongly hybridized with the conduction electron states in liquid Si. The width of virtual bound 3d states depends upon the density of states of conduction electrons at the Fermi level (E_F) and the strength of sp–d mixing [1]. Because of the large density of states of liquid Si at E_F, the TM solutes in liquid Si have a considerably large width of the virtual bound 3d states. It suggests that the whole of liquid TM–Si alloys may be in a non-magnetic state on the Si-rich side.

In the paper submitted [2], we have already obtained the magnetic susceptibility of liquid TM–Si alloys (TM = Mn, Fe, Co, Ni). There are few accurate data of magnetic susceptibility of Ti, V and Cr solutes in liquid metals. It is interesting to compare the behavior of Fe, Co and Ni solutes to those of Cr, V and Ti solutes. In this paper, the impurity susceptibility of the whole series of 3d metals in liquid Si will be studied. The trend of the impurity susceptibility obtained in liquid Si will be compared with those obtained in liquid Al, In and Sn [3–5]. The model of Anderson will be used to estimate the density of 3d states at E_F and the width of virtual bound 3d states.

2. Experimental procedure

Magnetic susceptibility measurements were made using a standard Faraday method with a torsion balance [2,5]. The field strength of the electromagnet was approximately 10 kOe with a 6 cm gap between the pole pieces. The constant value of $H(\mathrm{d}H/\mathrm{d}x)$ was 6.10 ± 0.15 (kOe)^2/cm. Mohr's salt with a room temperature susceptibility of 1.26×10^{-2} emu/mol was employed as a standard sample. Alloys of 0.5 g were put into alumina cells and were heated in a silicon carbide furnace in an atmosphere of high purity helium. The measurements were carried out during heating from the melting point up to a maximum temperature of around 1600 °C and also during the subsequent cooling process.

3. Results

Fig. 1 shows the magnetic susceptibility of liquid Ti–Si alloys as a function of temperature. For all composition up to 35 at.% Ti the magnetic susceptibilities were almost independent of temperature, which suggests that the Ti ions in the liquid alloys are in the non-magnetic state. The observed discontinuities on the low temperature side are due to solidification and are in accordance with the melting point given in literature (1480 °C at 35 at.% Ti) [6].

The magnetic susceptibilities as a function of temperature of liquid V–Si (up to 20 at.% V) and liquid Cr–Si (up to 50 at.% Cr) are shown in Figs. 2 and 3, respectively. As observed for the alloys of Ti–Si, the discontinuities of data are due to the onset of solidification and are again in accordance with the literature

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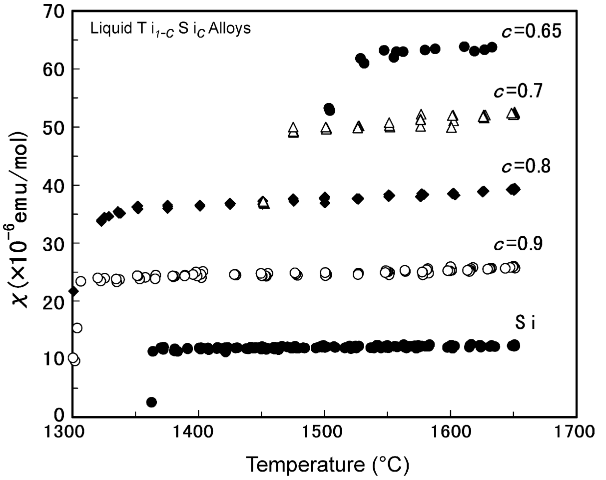

Fig. 1. Magnetic susceptibility of liquid Ti–Si alloys as a function of temperature.

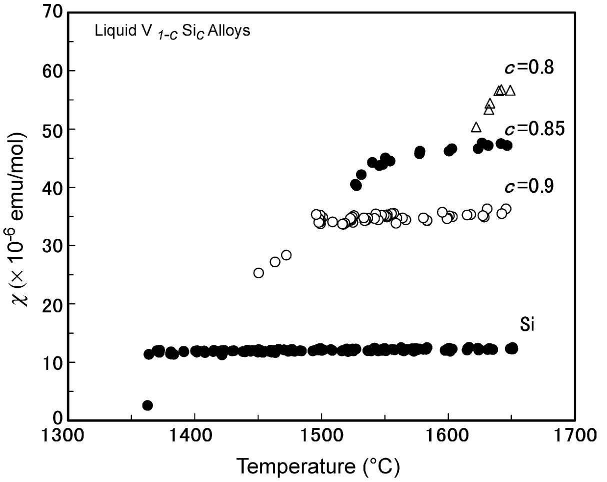

Fig. 2. Magnetic susceptibility of liquid V–Si alloys as a function of temperature.

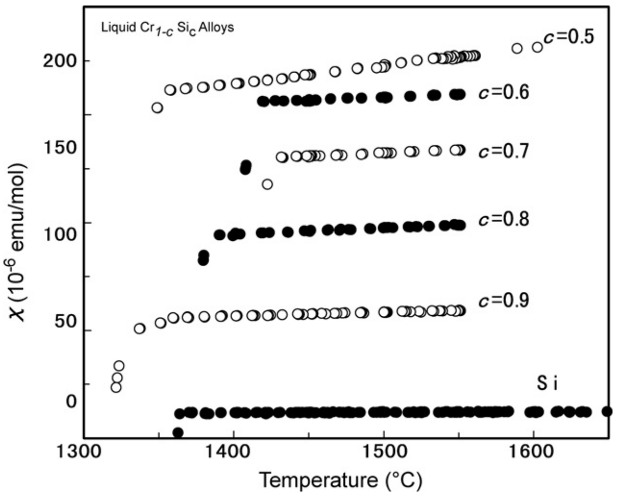

Fig. 3. Magnetic susceptibility of liquid Cr–Si alloys as a function of temperature.

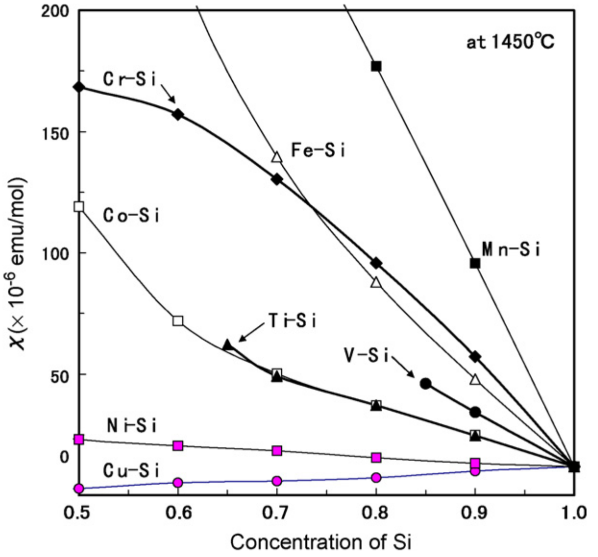

Fig. 4. Composition dependence of magnetic susceptibility in liquid 3d transition metal–Si alloys at 1450 °C. The values of liquid Mn, Fe, Co and Ni were taken from [2].

(1630 °C at 20 at.% V, 1350 °C at 50 at.% Cr) [6]. Similar to Ti–Si, the magnetic susceptibilities of both systems show a weak and positive temperature dependence of magnetic susceptibility, which suggests that both V and Cr ions in liquid Si are in a non-magnetic state.

Fig. 4 shows the composition dependence of susceptibility for the entire series of 3d metals at 1450 °C. The data of liquid TM–Si (TM = Mn, Fe, Co, Ni, Cu) were taken from the previous paper [2]. The increase in χ observed for small additions of less than half filled metals (10 at.% Cr, V, Ti) are larger than that for the corresponding more than half filled metals (10 at.% Fe, Co, Ni), respectively. That is, $\chi(\mathrm{Cr}) > \chi(\mathrm{Fe})$, $\chi(\mathrm{V}) > \chi(\mathrm{Co})$ and $\chi(\mathrm{Ti}) > \chi(\mathrm{Ni})$.

4. Discussion

The magnetic susceptibilities of liquid TM–Si alloys are given by [7]:

$$\chi = \chi_{3\mathrm{d}}(\mathrm{TM}^{+}) + \chi_{\mathrm{para}} + \{(1-c)\chi_{\mathrm{dia}}(\mathrm{TM}^{+}) + c\chi_{\mathrm{dia}}(\mathrm{Si}^{4+})\}, \tag{1}$$

where $\chi_{3\mathrm{d}}(\mathrm{TM}^{+})$ is the paramagnetic susceptibility due to the localized 3d electron states, and $\chi_{\mathrm{dia}}(\mathrm{TM}^{+})$ and $\chi_{\mathrm{dia}}(\mathrm{Si}^{4+})$ are the diamagnetic susceptibilities of the TM^{+} and Si^{4+} ion cores, respectively. It is known that Cu ions are monovalent in liquid metals. The assumption of TM^{+} ions is based upon the conclusions drawn from the alloying behavior of electronic properties of liquid TM–Ge (TM = Mn, Fe, Co, Ni, Cu) [8]. The diamagnetic value of Si^{4+} is -2.3×10^{-6} emu/mol [9], those of TM^{+} ions were interpolated from the trend of $\chi_{\mathrm{dia}}(\mathrm{TM}^{n+})$ as reported by [9]. The total values of diamagnetic susceptibility are shown in Table 1. The decrease in χ_{dia} due to the addition of 10 at.% TM solute lies in the range between -1.8 and -2.5×10^{-6} emu/mol.

Table 1

Experimental magnetic susceptibility $\chi_{(\mathrm{Exp.})}$, paramagnetic susceptibility χ_{para}, diamagnetic susceptibility χ_{dia} and impurity susceptibility $\chi_{3\mathrm{d}}$ of liquid $\mathrm{TM}_{0.1}\mathrm{Si}_{0.9}$ alloys

	$\mathrm{Ti}_{0.1}\mathrm{Si}_{0.9}$	$\mathrm{V}_{0.1}\mathrm{Si}_{0.9}$	$\mathrm{Cr}_{0.1}\mathrm{Si}_{0.9}$	$\mathrm{Mn}_{0.1}\mathrm{Si}_{0.9}$
$\chi_{(\mathrm{Exp.})}$	24.6	34.3	57.2	95.7
χ_{para}	13.5	13.3	13.3	13.4
χ_{dia}	−4.8	−4.7	−4.3	−4.4
$\chi_{3\mathrm{d}}$	15.9	25.7	48.2	86.7
	$\mathrm{Fe}_{0.1}\mathrm{Si}_{0.9}$	$\mathrm{Co}_{0.1}\mathrm{Si}_{0.9}$	$\mathrm{Ni}_{0.1}\mathrm{Si}_{0.9}$	$\mathrm{Cu}_{0.1}\mathrm{Si}_{0.9}$
$\chi_{(\mathrm{Exp.})}$	47.9	24.7	13.2	10.0
χ_{para}	13.3	13.3	13.3	13.1
χ_{dia}	−4.3	−4.2	−4.1	−3.6
$\chi_{3\mathrm{d}}$	38.9	15.6	4.1	0.5

Values are in ($\times 10^{-6}$ emu/mol).

The paramagnetic susceptibility, χ_{para}, due to the conduction electrons is given by [7,10]:

$$\chi_{\mathrm{para}} = \alpha(m^*, r_{\mathrm{s}})\mu_{\mathrm{B}}^2 N(E_{\mathrm{F}}), \tag{2}$$

where $N(E_{\mathrm{F}})$ is the density of states at E_{F}, which can be estimated from the nearly free electron model as follows:

$$N(E_{\mathrm{F}}) = \left(\frac{V}{2\pi^2}\right)\left(\frac{2m}{\hbar^2}\right)^{3/2} E_{\mathrm{F}}^{1/2} \tag{3}$$

here

$$E_{\mathrm{F}} = \left(\frac{\hbar^2}{2m}\right)\left(\frac{3\pi^2 N_{\mathrm{e}}}{V}\right), \tag{4}$$

where N_{e} is the number of conduction electrons.

The enhancement factor $\alpha(m^*, r_{\mathrm{s}})$ increases monotonously with effective mass, m^*, and inter-electron spacing r_{s}. The effective mass depends on the strength of electron–ion interaction.

For nearly free electrons the enhancement factor is given by the expression [7,10]:

$$\alpha(m^*, r_{\mathrm{s}}) = \frac{\alpha(r_{\mathrm{s}})}{[1 + \alpha(r_{\mathrm{s}})\{(m/m^*) - 1\}]} - \frac{m}{3m^*}. \tag{5}$$

For liquid Si the enhancement factor, $\alpha(r_{\mathrm{s}})$, calculated by random phase approximation is 1.23 [10]. The paramagnetic susceptibility of liquid Si obtained by subtracting $\chi_{\mathrm{dia}}(\mathrm{Si}^{4+})$ from the experimental value of 11.8×10^{-6} emu/mol amounts to approximately 14.1×10^{-6} emu/mol. With the help of $N(E_{\mathrm{F}})$ estimated from Eq.(3) and the value of χ_{para}, $\alpha(m^*, r_{\mathrm{s}})$ can be calculated from Eq. (2). The quantity m^*/m can be calculated from the values of $\alpha(r_{\mathrm{s}})$ and $\alpha(m^*, r_{\mathrm{s}})$ using Eq. (5). The values of $\alpha(m^*, r_{\mathrm{s}})$ and m^*/m are 0.97 and 1.07 for liquid Si, respectively. The average number of conduction electrons per ion decreases slightly from 4 to 3.7 with the addition of 10 at.% TM solute. $N(E_{\mathrm{F}})$ can be estimated from the average number of 3.7 per ion by using Eqs. (3) and (4). We estimate the values of χ_{para} under the assumption of a rigid band model assuming that the values of $\alpha(m^*, r_{\mathrm{s}})$ for liquid $\mathrm{TM}_{0.1}\mathrm{Si}_{0.9}$ are nearly equal to that for liquid Si. The values are shown in Table 1. As a result, the decrease in χ_{para} with the addition of 10 at.% TM solute lies in the range between −0.6 and -0.8×10^{-6} emu/mol.

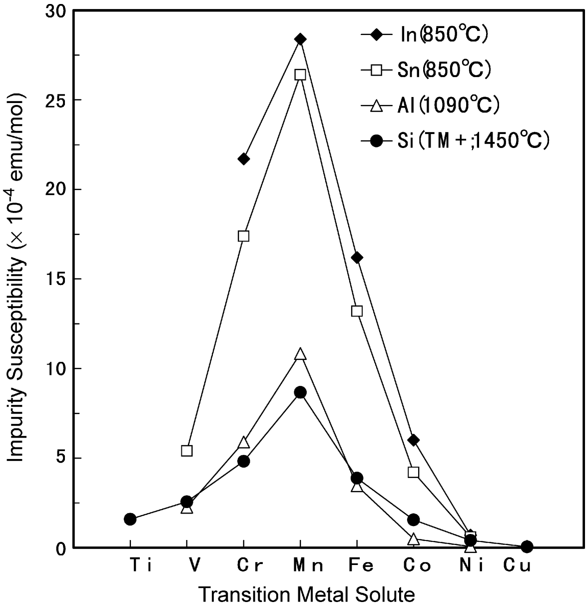

Fig. 5. Impurity susceptibility of 3d transition metal solutes in liquid Si at solute concentrations of 10 at.% TM. The data for host metals Al, In and Sn were taken from [3,5].

The values of the impurity susceptibility $\chi_{3\mathrm{d}}$ can be obtained by subtracting the χ_{para} and the total value of χ_{dia} from the experimental values of χ. Fig. 5 shows the variation of impurity susceptibility across the entire series in liquid Si together with the results of [3,5]. The trend of $\chi_{3\mathrm{d}}(\mathrm{TM}^{+})$ in liquid Si is similar to that in liquid Al, which also has the large value of $E_{\mathrm{F}} \approx 10.4$ eV. The peaks of impurity susceptibility in liquid Si and Al are considerably smaller than those in liquid In and Sn [4,5]. When Cr, Mn and Fe solutes are added into liquid metal solvents such as liquid Cu, Zn, In and Sn [5,11], the impurities are in the magnetic state in these liquid metals. In liquid Al solvent, however, the Cr, Mn and Fe ions are in the non-magnetic state as has been reported by Flynn et al. [3] and has been discussed in detail by Terzieff and co-workers [12,13]. In this work and the previous study [2], we have found a non-magnetic behavior of Cr, Mn and Fe ions in the wide composition range up to 50 at.% Cr, 40 at.% Mn and 50 at.% Fe for liquid Cr–Si, Mn–Si and Fe–Si, respectively.

According to the model of Anderson, the magnetic susceptibility of TM ions in the non-magnetic state is given by [1]:

$$\chi_{3\mathrm{d}} = N_{\mathrm{A}}\eta\mu_{\mathrm{B}}^2\rho_{\mathrm{d}}(E_{\mathrm{F}}). \tag{6}$$

Here η is the enhancement factor, defined by:

$$\eta = \left\{1 - \frac{(U + 4J)\rho_{\mathrm{d}}(E_{\mathrm{F}})}{10}\right\}^{-1}, \tag{7}$$

where $\rho_{\mathrm{d}}(E_{\mathrm{F}})$ is the density of d states at E_{F} and $U + 4J$ is the effective intra-atomic Coulomb and d–d exchange energy. As shown in Fig. 6, the parameter $(U + 4J)$ decreases with increasing E_{F} [8]. E_{F} of liquid Si estimated from Eq. (4) is as large as 13.4 eV [14]. Therefore, the reasonable value of $(U + 4J)$ is

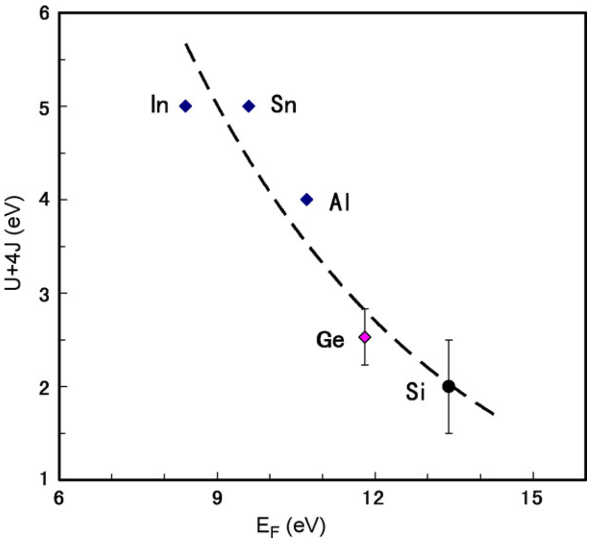

Fig. 6. Effective intra-atomic d–d Coulomb and exchange interaction energy of 3d transition metal solutes vs. E_F in liquid Si (this paper) and In, Sn, Al, Ge taken from [5,8].

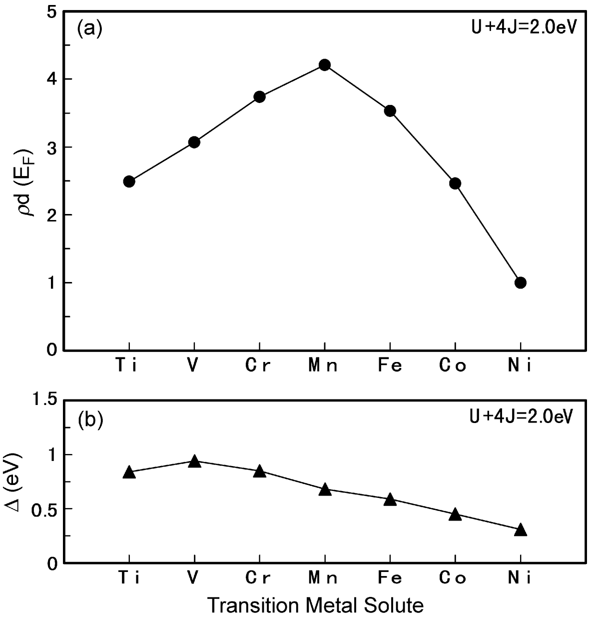

Fig. 7. (a) Density of d states, $\rho_d(E_F)$, of 3d impurities in liquid Si and (b) width of virtual bound 3d states of 3d impurities in liquid Si.

1.5–2.5 eV for transition metal solutes in liquid Si. Assuming that the value of $(U+4J)$ is 2.0 eV, we can estimate the values of $\rho_d(E_F)$ with the help of the known values of the impurity susceptibility. The variation of $\rho_d(E_F)$ is shown in Fig. 7a.

In the non-magnetic case, the density of d states is given by [1]:

$$\rho_d(E_F) = \frac{(10\Delta/\pi)}{\{(E_F - E_d)^2 + \Delta^2\}} = \left(\frac{10}{\pi\Delta}\right)\sin^2\left(\frac{\pi N_d}{10}\right), \quad (8)$$

where N_d and E_d are the number and the energy level of the localized 3d electrons, respectively. Δ is the width parameter of the virtual bound 3d states which depends on the $N(E_F)$ of the solvent and the strength of sp–d mixing, defined by:

$$\Delta = \pi|V_{d,sp}|^2 N(E_F), \quad (9)$$

where $V_{d,sp}$ is the sp–d admixture matrix element. Based on the assumption of monovalent transition metals, we can estimate the values of Δ from the $\rho_d(E_F)$ by using Eq. (8) and therewith $V_{d,sp}$ can be deduced from Eq. (9). As shown in Fig. 7b, Δ decreases gradually across the 3d series from V to Ni. As a result, by the virtue of Eq. (9) $V_{d,sp}$ decreases gradually with increasing the number of localized 3d electrons. The enhancement factor η estimated for the liquid Si solvent is 2.0, 2.6, 4.0, 6.4, 3.4, 2.0 and 1.2 for Ti, V, Cr, Mn, Fe, Co and Ni solutes, respectively. The enhancement of Cr, Mn and Fe is considerably larger than that of Ti, V, Co and Ni. Their large values suggest that the magnetic behavior of Cr, Mn and Fe is reasonable in liquid Cu, In and Sn. According to the calculation of Eqs. (3) and (4), the behavior of non-magnetic Cr, Mn and Fe solutes in liquid Si are closely related to the large density of states at E_F of liquid Si.

5. Conclusion

The magnetic susceptibilities of liquid $TM_{0.1}Si_{0.9}$ alloys (TM = Ti–Ni) are almost independent of temperature, which suggests that the transition metal atoms are in the non-magnetic state in liquid Si. The impurity susceptibility was estimated by subtracting the paramagnetic susceptibility of conduction electrons and the diamagnetic susceptibility of ions from the experimental value of χ. The trend of impurity susceptibility shows a sharp peak around Mn. The trend in liquid Si, which is related to the large value of E_F is considerably less pronounced than those in liquid In and Sn. The values of $\rho_d(E_F)$ can be estimated from the impurity susceptibility under the assumptions that $(U+4J)$ is 2.0 eV and that transition metal solutes are monovalent in liquid Si. The width parameter was found to decrease gradually across the series from V to Ni solute.

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