Heat Capacity Studies of Ni Substituted FeSi

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Abstract. Heat capacity measurements of Ni substituted FeSi has been presented in this report. Iron Silicide (FeSi) is one of the fascinating semiconductors among cubic hybridized semiconductors. Energy gap in FeSi is very sensitive with external impurities.Ground state properties of FeSi could be modified by using various substitutions. In this report we have shown the implications of impurity states formation at very low level doping (x = 0.005) as well as for higher doping comparable to metal-insulator transitionconcentrations (x = 0.02, 0.04) through calorimetric studies.

INTRODUCTION

Semiconductors contribution are enormous in electronics industriesincluding spintronicsand knowledge of transport properties are necessary. It gives basic model to theorize transport properties at absolute zero. Scientific community are always have a keen interest in semiconductors due to its unusual nature of transport behavior by external parameters. Physical properties of semiconductor at low temperatures are exotic and anomalous due to finite impurities present in it. So it is necessary to study impurity effects on transport properties at low temperatures. MIT is one fascinating physical phenomena that has been studied over several decades. Physical properties around MIT helps to understand how transport property are greatly affected by external parameters such as magnetic field, impurities, pressure and so on. Classical semiconductors such as Silicon (Si) or Germanium (Ge) are rigorously studied under above external conditions over past several decades and their physical properties are well analyzed with various impurities such as Al, P, As. FeSi is a hybridized semiconductor whose physical properties are exotic at low temperatures. Alloying of transition metal iron and metalloid silicon makes a unique material whose behavior neither as metal nor completely as semiconductor. FeSi crystallizes B20 cubic form with space group $P2_13$. Each unit cell of FeSi contains eight atoms. Exotic properties of ground state is connected with non-centrosymmetric arrangement of Fe and Si atoms in unit cell [1]. At room temperatures FeSi behaves like metallic whereas while cooling to low temperatures it changes to activated behavior due to gap opening around Fermi level. FeSi is paramagnetic metal at high temperatures above ~400 K but when decreasing temperature resistivity increase and saturates below 10 KEnergy gap of FeSi is 50 meV at low temperatures [2] [3].

Researchers suggest that appearance of non-magnetic singlet ground state at low temperatures is of Kondo type but still debate going on. Ground state of this system is distinct in the sense that electronics properties cannot be accounted with classical semiconductor model. The ground state of system is very sensitive with external impurities. Co doped FeSi gives itinerant ferromagnetic system, a non-Fermi liquid can be derived with Mn as impurities. Ge is similar electronic configuration as Si and by substituted in Si site makes ferromagnetic metal. FeSi and CrSi are paramagnetic metal, MnSi is itinerant ferromagnet and CoSi is diamagnetic metal [4]. All these variety of ground states can be achieved with transition from semi conducting to metallic nature at low temperatures with various dopant. So by understanding formation of impurity states around Fermi level will help to gain knowledge on ground state properties as well as impurity effects at low temperatures. A thermodynamic investigation is suitable to gather knowledge of above said problem.

EXPERIMENTAL METHODS

Samples have been prepared by using arc melting technique in argon environment that are in polycrystalline nature. High purity elements of Iron, Silicon and Nickel ingots have been taken as per required ratio and melted in rod shape. Titanium ball have been used as a getter element to observe residual gases and improve better vacuum. Derived polycrystalline samples are sealed in evacuated quartz at high vacuum better than 10^{-5} bar and annealed for a week at 1000 degree Celsius. This will improve sample homogeneity and relieve stress that might be occurred while fast cooling melted samples followed by sudden melting.Heat capacity study has been done by relaxation time approximation on QD-PPMS 14 T from 2-300K on various doping concentrations.Size of samples has been reduced and polished in-order fit inside of heat capacity puckplatform.

RESULTS AND DISCUSSIONS

Heat capacity of $Fe_{1-x}Ni_xSi$

In Figure 1(a) we have shown heat capacity measurements of Ni substituted FeSi at zero field.Substitution of Ni impurity on Fe site have two more valence electrons compare to Fe. Figure 1 (a) insets shows value of C_m increases with increasing Ni substitution at low temperatures and this could be due to contributions of impurity spin entropy anda broad hump around 5 K is observed in all Ni substituted samples indicating large excess specific heat.Heat capacity below 30 K are well fitted with sum of contributions of electronic, lattice and two level system of schottky effect. At low temperatures below 10 K a schottky contribution is seen whose fits are quite good. Theseschottky contributions are due to excitations within two levels consists of energy separation Δ. Equation that has been used for fittings are as follows [5]

$$C_p = \gamma T + \beta T^3 + \delta T^5 + A\left(\frac{\Delta}{k_B T}\right)^2 \left(1+\exp\left(\frac{\Delta}{k_B T}\right)\right)^{-2} \exp\left(\frac{\Delta}{k_B T}\right) \quad 1)$$

Here γ is sommerfeld coefficient, Δ/k_B is energy gap of two level system. Debye temperature Θ_D can be derived from T^3 coefficient β and value of $\Theta_D$can be calculated from following equation $\theta_D = \left(\frac{12\pi^4 Rn}{5\beta}\right)^{1/3}$.β = 0.00948 and is almost constant for all doping concentrations means Θ_D= 742.4 K whichisnot varying irrespective of doping concentrations.Parameters from fitting are tabulated in table 1 which shows the energy separation changes non-monotonically and the sommerfeld coefficients increases gradually from x = 0.005 to x = 0.04. The sommerfeld coefficients suggests that considerable mass enhancement with increasing doping concentrations and Ni impurity states are formed around Fermi level which is the most interesting scenario among hybridized insulators including rare earths. Physical properties of Ni substituted FeSi are depends on d-states that has been formed around Fermi level.

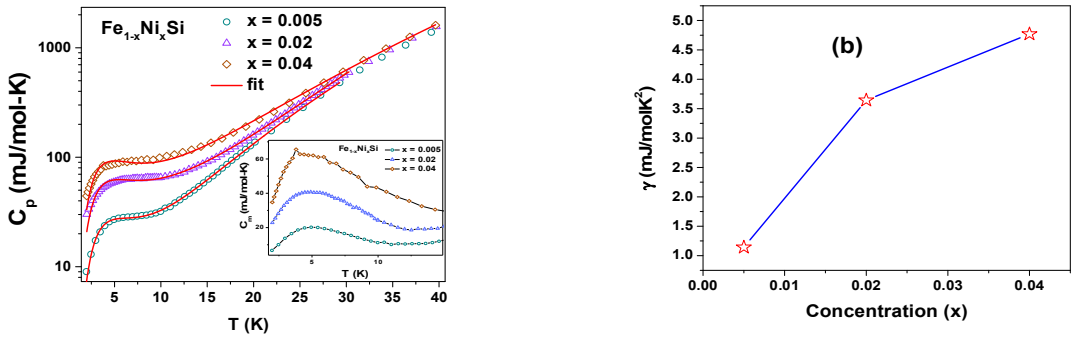

FIGURE 1.(a) Log plot heatcapacity (HC)vs temperature of $Fe_{1-x}Ni_xSi$ (x = 0.005, 0.02, 0.04) at zero field of low temperatures below 40 K. Inset: HC at low temperature below 10 K of $Fe_{1-x}Ni_xSi$. (b) Somerfeld coefficient (γ) of $Fe_{1-x}Ni_xSi$ vs concentration.

TABLE 1. Values of Schottky energy interval and Sommerfeld coefficients tabulated for $Fe_{1-x}Ni_xSi$.

$Fe_{1-x}Ni_xSi$	Schottky energy interval (Δ/k_B) (K)	Sommerfeld coefficient (γ mJ/mol-K^2)
x = 0.005	11.3	1.14
x = 0.02	10.7	3.64
x = 0.04	10.3	10.33

Magnetic entropy (S_m) has been calculated by using equation 2 and shown in figure 1 (b). S_m increases with increasing Ni concentration and saturates above 15 K. As compared to x = 0.005 (184 mJ/mol-K^2 at 15 K), S_m of x = 0.04 (622 mJ/mol-K^2 at 15 K) has been increased around three times and this could be due to additional impurities of Ni that has been added.

$$S_m = \int \frac{C_m}{T} dT \qquad 2)$$

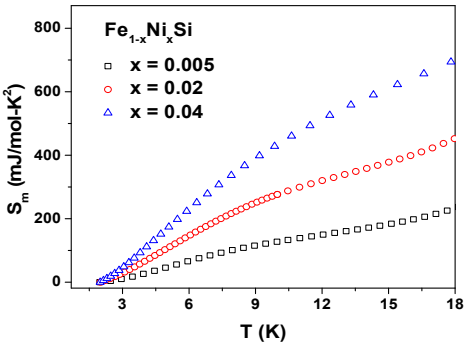

FIGURE 2. Magnetic entropy of $Fe_{1-x}Ni_xSi$ (x = 0.005, 0.02, 0.04) at low temperatures.

CONCLUSION

Heat capacity of Ni substituted FeSi has been studied and presented in this report. Increasing Sommerfeld coefficient suggest that Ni impurities introduces d-states around Fermi level and physical and ground state properties are dependson these impurity states at low temperatures. Debye temperature Θ_D= 742.4 K and is not effectively varying with doping of Ni. Magnetic entropy that has been calculated from equation (2) is increases with increasing Ni concentration around three times.

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