Chapter 6

The normal state properties of the Ti-V alloys

6.1 Introduction

In the chapter 4, we have observed that for the Ti$_x$V$_{1-x}$ alloys with concentrations $x = 0.4$, 0.6 and 0.7, the experimentally determined superconducting transition temperature $T_C$ is significantly lower than that estimated using McMillan formula [19]. We have also pointed out that the presence of soft-phonon modes and/or spin fluctuations in a material may lead to such a disagreement between the experimental and theoretical values of $T_C$. In this chapter, we present the results of our study on the various normal state properties of these Ti-V alloys to understand the possible reasons behind this difference between the experimental and theoretical values of $T_C$. Our studies on the temperature dependence of heat capacity, dc magnetic susceptibility and electrical resistivity indicate the presence of spin fluctuations in the Ti-V alloys, particularly in those having higher V concentration. This is
further supported by the observed enhanced Stoner factor and the validity of the Kadowaki-Woods scaling relation [180] for these Ti-V alloys. Based on these experimental observations we infer that lower value of the experimentally observed \(T_C\) as compared to that estimated using McMillan formula is due to the strong pair-breaking effect of the spin fluctuations. On the basis of their theoretical study [93], Pictec et al. had also made a similar inference. Our study reveals that the presence of spin fluctuations in Ti-V alloys not only explains the difference between the experimental and theoretical values of \(T_C\), but also accounts for the non-monotonic variation of \(T_C\) as a function of \(x\) in the Ti\(_x\)V\(_{1-x}\) alloys.

![Graphs](image)

Figure 6.1: (a) The temperature dependence of heat capacity in the temperature range 2-225 K for the Ti-V alloys. The solid lines are the best-fit curves based on the relation \(C(T) = \gamma T + C_L\) (see text for details). (b) The temperature dependence of heat capacity of the Ti-V alloys presented in \(C/T\) versus \(T^2\) fashion in the temperature range 2-35 K. The non linearity in the \(C/T\) versus \(T^2\) plots observed in this temperature range indicates the presence of soft-phonon modes or spin fluctuations in these Ti-V alloys.

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6.2 Results and discussion

6.2.1 The temperature dependence of heat capacity of the Ti-V alloys

In Fig. 6.1(a) we show the temperature dependence of heat capacity for the Ti-V alloys in the temperature range 2-225 K. In this figure, the scale on the y-axis actually corresponds to the heat capacity of the Ti$_{0.4}$V$_{0.6}$ alloy only. The rest of the curves are shifted upwards (so as to create a difference of 5 J/mole-K between any two of the curves at the lowest temperature of measurement) for better clarity. In this figure the solid lines are the fits to the experimental data based on the relation $C(T) = \gamma T + C_L$, where $C_L$ represents the Debye lattice heat capacity which is given by

$$C_L(T) = 9R \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D} \frac{x^4 e^x}{(e^x - 1)^2} dx.$$  \hspace{1cm} (6.1)

Here, $R$ is the universal gas constant and $\theta_D$ is the Debye temperature. For performing the fitting, we take $\theta_D$ and the Sommerfeld coefficient $\gamma$ as the fitting parameters. It is evident from Fig. 6.1(a) that the fitting degrades at low temperatures, and the observed disagreement between the experiment data and the theory becomes more prominent as the V concentration in these Ti-V alloys is increased. Such a disagreement between the experimental $C(T)$ data and the theory may arise from using of a single value of $\theta_D$ to fit the $C(T)$ data in a large temperature range. However, our thermal expansion measurement on the Ti$_{0.6}$V$_{0.4}$ alloy indicates that the variation of $\theta_D$ in the
temperature range from 4.2 K to 300 K is less than 10 % (the experimental data are not shown here). We have found that the observed disagreement between the experimental $C(T)$ data and the theory cannot be accounted by such a small variation in $\theta_D$. In Fig. 6.1(b) we show the plots of $C/T$ as a function of $T^2$ for the present Ti-V alloys in the temperature range 2-35 K. A non-linearity with a negative curvature is observed in these plots, indicating the presence of low energy excitations such as soft-phonons [118, 120, 181] or spin fluctuations [119, 120] in the Ti-V alloys. In the case of soft-phonons or spin fluctuations, a simplified model has been used in the literature, in which the phonon density of states $F(\omega)$ are represented by a set of Einstein modes (with frequency $\omega$) having constant spacing in the logarithmic frequency scale [118]. This simplified model does not give the detailed map of the phonon density of states that is generally obtained through the neutron scattering experiments but rather produces a smooth phonon distribution function $F(\omega)$. It is reported in literature that certain functional of the lattice heat capacity may be used to represent the form of such phonon spectrum [118]. One such functional $(5/4)\pi^4C_LT^3$ is an image of the spectrum $\omega^{-2}F(\omega)$ for $\omega = 4.928T$, where $\omega$ is expressed in Kelvin. In this model, $F(\omega)$ is given by [118]

$$F(\omega) = \sum_k F_k \delta(\omega - \omega_k). \quad (6.2)$$

Using this representation, the lattice heat capacity $C_L$ is then given by [118]
\[ C_L = 3R \sum_k F_k(z_k)^2 e^{z_k}/[e^{z_k} - 1]^2. \] (6.3)

Where, \( z_k = \omega_k/T \) and \( F_k \) is the weight factor for the \( \omega_k \). The value of \( k \) is so chosen that the least number of terms is sufficient to fit the experimental heat capacity data. Then \( F_k \) is determined by the least square fit with a condition \( \sum_k F_k = 1 \). We adopt this model to understand the temperature dependence of heat capacity in the normal state of the present Ti-V alloys.

Figure 6.2: The plots of \( C_L T^{-3} \) as a function of \( \ln(4.928T) \) (indicated by the open symbols with a large density of points) and \((4/5)R\pi^2\omega^{-2}F(\omega)\) as a function of \( \ln(\omega) \) (dotted bar curves) for the Ti-V alloys.

Fig. 6.2 shows the plots of \( C_L T^{-3} = (C - \gamma T)/T^3 \) as a function of \( \ln(4.928T) \) for the present Ti-V alloys. The presence of soft-phonon or spin
fluctuations in these alloys is indicated by the increase in $C_L T^{-3}$ at low values of $\ln(4.928T)$. The temperature dependence of $C_L$ is fitted with the above equation by considering 10 Einstein frequencies ($k=10$). The correspondence between the fit and the data is shown by plotting $(4/5)R\pi^2\omega^{-2}F(\omega)$ as a function of $\ln(\omega)$ along with the plot of $C_L T^{-3}$ against $\ln(4.928T)$. Then the characteristic phonon scaling frequency $\bar{\omega}_{\text{log}}$ is estimated as [119]:

$$\bar{\omega}_{\text{log}} = \exp \left[ \frac{\int d(ln\omega)F(\omega)ln(\omega)}{\int d(ln\omega)F(\omega)} \right].$$

The obtained value of $\bar{\omega}_{\text{log}}$ can be used to estimate $T_C$ from the Allen-Dynes form [6.8] of the McMillan formula [19] as

$$T_C = \frac{\bar{\omega}_{\text{log}}}{1.2} e^{\exp \left[ \frac{-1.04(1 + \lambda_{ep})}{\lambda_{ep} - \mu^*(1 + 0.62\lambda_{ep})} \right]}.$$  \hspace{1cm} (6.5)

In Table 6.1, we present the values of $\bar{\omega}_{\text{log}}$ and the corresponding $T_C$ values for all the present Ti-V alloys estimated using $\mu^* = 0.12$ and $\lambda_{ep}$ values obtained from the heat capacity data (given in Table 4.1). In chapter 4, we have shown that the value of $\mu^*$ is about 0.12 for the Ti-V alloys, and such a value of $\mu^*$ is commonly used for all the transition metals and their alloys. We find that for the $\text{Ti}_x\text{V}_{1-x}$ alloys having concentrations $x = 0.4$, 0.6 and 0.7, the value of $T_C$ estimated using expression (6.5) is still higher than that obtained experimentally. Hence, the existence of soft-phonons in these Ti-V alloys cannot explain the observed low value of the experimentally $T_C$ of these alloys. We therefore explore the possibility of the existence of
spin fluctuations [92, 183] in these Ti-V alloys, which also could lead to a suppression of $T_C$. In this direction, we now present the results of our studies on the temperature dependence of dc magnetic susceptibility and electrical resistivity in the normal state of these alloys.

Table 6.1: $T_C$ of the Ti-V alloys estimated with the help of the Allen-Dynes form of the McMillan formula using $\mu^*=0.12$ and, $\bar{\omega}_{log}$ and $\lambda_{ep}$ obtained from the heat capacity data. The values of $\bar{\omega}_{log}$ obtained from the analysis of the heat capacity data are also given.

<table>
<thead>
<tr>
<th></th>
<th>Ti$<em>{0.4}$V$</em>{0.6}$</th>
<th>Ti$<em>{0.6}$V$</em>{0.4}$</th>
<th>Ti$<em>{0.7}$V$</em>{0.3}$</th>
<th>Ti$<em>{0.8}$V$</em>{0.2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{\omega}_{log}$ (K)</td>
<td>226.3</td>
<td>221.3</td>
<td>235.8</td>
<td>243.5</td>
</tr>
<tr>
<td>$T_C$ (K)</td>
<td>18.9</td>
<td>11.8</td>
<td>10.7</td>
<td>4.2</td>
</tr>
</tbody>
</table>

6.2.2 The temperature dependence of magnetic susceptibility of the Ti-V alloys

Fig. 6.3 shows the temperature dependence of dc magnetic susceptibility $\chi = M/H$ for the Ti-V alloys in the temperature range 10-300 K. The magnetization ($M$) was measured in the presence of 1 T magnetic field using a SQUID magnetometer. The data were corrected for the background signal. For doing this, the SQUID profiles were measured first for the bare sample holder (empty straw) at the temperatures and magnetic fields where the measurements were to be performed on the sample. Then the sample was inserted into the straw keeping the configuration of the straw same, and then the SQUID profiles were obtained at the same temperatures and
Figure 6.3: Temperature dependence of dc magnetic susceptibility $\chi$ for the Ti-V alloys in the temperature range 10-300 K. A peak in the $\chi(T)$ curve is observed at $T \sim 200$ K for Ti$_{0.4}$V$_{0.6}$ alloy. The peak shifts to higher temperatures and the magnitude of $\chi$ decreases with increasing Ti concentration. The solid lines represent the fitting based on the Eqn. 1.7.

magnetic fields where the profiles of the empty straw were recorded. The SQUID profiles for the empty straw were then subtracted from the SQUID profiles for the sample plus straw configuration, before fitting the profiles for the estimation of the magnetic moment. Magnetic susceptibility in all the present Ti-V alloys increases with the increase in temperature. Such behaviour is termed as “temperature induced magnetism” which is unlike that of a paramagnet where the susceptibility decreases with increasing temperature. The temperature induced magnetism observed in various transition metals is reported to occur due to the temperature dependence of the Pauli paramagnetism [184]. The temperature dependence of Pauli paramagnetism
can be expressed within the Fermi liquid picture as [185]:

\[
\chi(T) = \chi_P \left[ 1 + \frac{1}{6} \pi^2 (k_B T)^2 \left( \frac{1}{n \delta E} \right)_{E_F}^2 \left( \frac{1}{\delta n / \delta E} \right)_{E_F}^2 \right].
\] (6.6)

Here, \( n = N(0) \) is the bare electron density of states (DOS) at the Fermi energy \( E_F \), which has been estimated for the present Ti-V alloys using the band structure calculations (refer to chapter 4). The plots of the bare electronic density of state of the Ti-V alloys as a function of energy (Fig. 4.3 of chapter 4) are used to estimate the quantities \( (\delta^2 n / \delta E^2) \) and \( (\delta n / \delta E) \) at \( E_F \). The results of these estimations indicate that the coefficient of the \( T^2 \) term in the above equation is negative for the Ti\(_x\)V\(_{1-x}\) alloys having compositions \( x = 0.4 \) and 0.6. This will lead to a decrease in \( \chi \) with the increase in temperature, which is not observed experimentally. However, our studies on electronic structure show that the bare electron density of states at the Fermi energy is very large and are dominated by 3\(d\) electrons. In such case, the Pauli susceptibility is enhanced due to the spin fluctuations, and the temperature dependence of \( \chi \) follows the relation [186, 187]

\[
\chi(T) = \chi(0) - bT^2 \ln \left( \frac{T}{T'} \right),
\] (6.7)

where, \( \chi(0) \), \( b \), and \( T' \) are constants. The characteristic temperature \( T' \) is related to the characteristic temperature \( T_P \) at which a peak in the temperature dependence of susceptibility occurs, as: \( T_P = T'/e^{\frac{1}{2}} \) [186, 187]. The
above equation nicely fits the $\chi(T)$ data of the present Ti-V alloys (Fig. 6.3). The values of $\chi(0)$, $b$, and $T'$ obtained as the fitting parameters are presented in Table 6.2. It is observed that $\chi(0)$ decreases with the increase in Ti concentration $x$ in the Ti$_x$V$_{1-x}$ alloys, whereas $T'$ increases as $x$ increases. It is also observed that the temperature dependence of susceptibility approaches $T^2$ behaviour as $x$ increases. This can be interpreted as an indication that the system approaches toward Fermi liquid behaviour with increasing $x$. A small Curie tail is observed at low temperatures, which may be related to a small amount paramagnetic impurities (not detectable in the XRD measurements) present in theses alloys. The isothermal field dependence of magnetization at various constant temperatures above 10 K does not show any indication of saturation even in 8 T applied magnetic field, and thereby ruling out any appreciable contribution from ferromagnetic impurities.

We estimate Pauli spin susceptibility $\chi^P$ from the bare electronic density of states at the Fermi energy using the relation $\chi^P = \mu_0 \mu_B^2 N(0)$, where $\mu_B$ is the Bohr magneton and $\mu_0$ is the permeability of the free space. This estimate is almost an order of magnitude lower than the experimental magnetic susceptibility $\chi_{exp}[= \chi(0)/\mu_0]$, indicating that these Ti-V alloys are enhanced Pauli paramagnets. In such cases, the Stoner enhancement factor $S$ can be estimated as

$$S = \frac{\chi_{exp}^P}{\chi^P}.$$  \hspace{1cm} (6.8)

Here $\chi_{exp}^P$ is the experimentally obtained Pauli spin susceptibility. In order
Table 6.2: Various parameters estimated from the temperature dependence of dc magnetic susceptibility of the Ti-V alloys in their normal state. The parameter $T_{sf}$ is obtained from the temperature dependence of resistivity of the Ti-V alloys in their normal state.

<table>
<thead>
<tr>
<th></th>
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<th>Ti$<em>{0.7}$V$</em>{0.3}$</th>
<th>Ti$<em>{0.8}$V$</em>{0.2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi(0)$ (10$^{-10}$ Wb/A)</td>
<td>5.13±0.03</td>
<td>4.88±0.003</td>
<td>3.55±0.007</td>
<td>3.04±0.003</td>
</tr>
<tr>
<td>$b$ (10$^{-10}$Wb/A-K$^2$)</td>
<td>2.27±0.6</td>
<td>3.85±0.17</td>
<td>4.91±0.28</td>
<td>4.51±0.06</td>
</tr>
<tr>
<td>$T'$ (K)</td>
<td>372±15</td>
<td>512±12</td>
<td>616±19</td>
<td>757±9</td>
</tr>
<tr>
<td>$\chi_{exp}$ (10$^{-4}$ unit less)</td>
<td>4.08±0.026</td>
<td>3.88±0.0024</td>
<td>2.82±0.005</td>
<td>2.42±0.002</td>
</tr>
<tr>
<td>$\chi_{P}^{exp}$ (10$^{-4}$ unit less)</td>
<td>1.81±0.01</td>
<td>1.99±0.001</td>
<td>1.12±0.002</td>
<td>9.08±0.001</td>
</tr>
<tr>
<td>Stoner factor $S$</td>
<td>~2.04</td>
<td>~2.28</td>
<td>~1.40</td>
<td>~1.18</td>
</tr>
<tr>
<td>Wilson’s coefficient $R_W$</td>
<td>~1.2</td>
<td>~1.5</td>
<td>~0.94</td>
<td>~0.93</td>
</tr>
<tr>
<td>$T_{sf}$ (K)</td>
<td>~155</td>
<td>~90</td>
<td>~70</td>
<td>···</td>
</tr>
</tbody>
</table>

Table 6.2: Various parameters estimated from the temperature dependence of dc magnetic susceptibility of the Ti-V alloys in their normal state. The parameter $T_{sf}$ is obtained from the temperature dependence of resistivity of the Ti-V alloys in their normal state.

to estimate $\chi_{P}^{exp}$ from $\chi_{exp}$, one needs to know the orbital susceptibility $\chi_{O}^{exp}$. However, the estimation of $\chi_{O}^{exp}$ from the experimental data is rather difficult. We have taken the values of $\chi_{O}^{exp}$ of the end members of the Ti-V system from the literature. These values are reported to be $\chi_{O}^{exp} \sim 1.14 \times 10^{-4}$ for $\beta$-Ti and $\chi_{O}^{exp} \sim 3.02 \times 10^{-4}$ for $\beta$-V [117]. Linear interpolation between these two end-values is used to estimate $\chi_{O}^{exp}$ for the present alloy compositions. Then $\chi_{exp}^{P}$ values for the present Ti-V alloys are obtained by subtracting $\chi_{O}^{exp}$ from $\chi_{exp}$, and these values are given in Table 6.2. The estimated value of $S$ is $\sim 2$ (Table 6.2) for the V-rich Ti-V alloys, indicating the relevance of spin fluctuations in these alloys. On the other hand, $S \sim 1$ for Ti$_{0.8}$V$_{0.2}$ alloy, indicating that the spin fluctuations are suppressed in Ti-rich Ti-V alloys. We have also estimated the Wilson’s coefficient $R_W$ for the present Ti-V alloys using the
relation: \( R_W = \left( \frac{\pi^2 k_B^2}{3\mu_B^2} \right) \frac{\chi^{\text{exp}}}{\gamma} \) [188]. The values of the Wilson’s coefficient \( R_W \) for the present Ti-V alloys are also given in Table 6.2. We observe that \( R_W > 1 \) for the Ti\(_x\)V\(_{1-x}\) alloys having concentration \( x = 0.4 \) and 0.6, indicating that these alloys are strongly correlated systems where spin fluctuations are enhanced [188].

![Figure 6.4](image)

**Figure 6.4:** Temperature dependence of resistivity of the Ti-V alloys measured in zero applied magnetic field and in temperature range 10-300 K.

### 6.2.3 Electrical resistivity of the Ti-V alloys

The temperature dependence of electrical resistivity (\( \rho \)) for the present Ti-V alloys in the temperature range 10-300 K is shown in Fig. 6.4. The magnitude as well as the temperature dependence of resistivity of these Ti-V alloys is
observed to depend strongly on the alloy composition. For the Ti$_x$V$_{1-x}$ alloys having concentrations $x = 0.4$ and 0.6, resistivity increases with the increase in temperature in the entire temperature range of measurement. For both these alloys, resistivity shows linear temperature dependence at high temperatures, and a deviation from this linear behaviour is observed at low temperatures. In the main panel of Fig. 6.5(a), the observed linearity of the plot of $(\rho - \rho_0)$ against $T^2$ for the Ti$_x$V$_{1-x}$ alloys with $x = 0.4$ and 0.6 indicates a quadratic temperature dependence of resistivity of these alloys at low temperatures. Such a quadratic temperature dependence of resistivity at low temperature is commonly exhibited by the materials where the strong presence of spin fluctuations is observed.

Figure 6.5: (a) Resistivity $\rho$ versus $T^2$ plots for the Ti$_{0.4}$V$_{0.6}$ and Ti$_{0.6}$V$_{0.4}$ alloys showing the $T^2$ dependence of resistivity at low temperatures (20-45 K). The inset of (a) show the plot of $(\rho - \rho_0)/T^2$ against $T^3$ for the Ti$_{0.4}$V$_{0.6}$ alloy to illustrate the relevance of the $T^5$ term in the $\rho(T)$ data. (b) The plot of the temperature dependence of resistivity for the Ti$_{0.7}$V$_{0.3}$ alloy, where temperature is plotted in log scale. Its inset shows that the $\rho(T)$ of this alloy remains unaffected on the application of magnetic field.
Although the function $\rho(T) = \rho_0 + AT^2$ well describes the temperature dependence of resistivity of the Ti$_x$V$_{1-x}$ alloys having concentrations $x = 0.4$ and $0.6$ at low temperatures, the fitting improves significantly when an additional $T^5$ term is considered in the fitted function. The $T^5$ dependence of resistivity at low temperatures is known to arise from the electron-phonon scattering mechanism. The plot of $(\rho - \rho_0)/T^2$ as a function of $T^3$ is shown in the inset to Fig. 6.5(a) for the Ti$_{0.4}$V$_{0.6}$ alloy. The observed weak slope of this plot indicates that the $T^5$ term has some relevance in the temperature dependence of resistivity of this alloy at low temperatures, though the coefficient of the $T^5$ term is very small ($\sim 10^{-9} \mu \Omega\cdot\text{cm-K}^{-5}$) for this alloy. The coefficient of the $T^5$ term is also found to be very small but negative for the Ti$_{0.6}$V$_{0.4}$ alloy. The negative as well as the small value of the coefficient of $T^5$ term can be explained within the theoretical models of electrical resistivity which consider the contribution arises from the scattering mechanism between the conduction electrons and the spin fluctuations [189, 190].

The temperature dependence of resistivity arising from the scattering of the conduction electrons by spin fluctuations can be expressed as [189, 190]

$$\rho_{sf}(T) = a \left( \frac{T}{T_{sf}} \right)^2 \left[ J_2 \left( \frac{T_{sf}}{T} \right) - \left( \frac{T}{T_{sf}} \right)^3 J_5 \left( \frac{T_{sf}}{T} \right) \right]. \quad (6.9)$$

Here, $a$ is an arbitrary constant, $T_{sf}$ is the characteristic spin-fluctuations temperature and $J_n$’s are the standard Bloch-Gruneisen scattering integrals. On the other hand, the contribution to the resistivity at low temperatures,
arising from the electron-phonon interactions, is given by [189, 190]

\[ \rho_{ph}(T) = b \left( \frac{T}{\theta_D} \right)^5 J_5 \left( \frac{\theta_D}{T} \right) \tag{6.10} \]

where, \( b \) is some constant and \( \theta_D \) is the Debye temperature. Then the total ideal resistivity at low temperatures will be obtained by combining the above two contributions, and is given as

\[ \rho(T) = \rho_{sf}(T) + \rho_{sf}(T) = \left( \frac{a}{T_{sf}^2} \right) J_2 \left( \frac{T_{sf}}{T} \right) T^2 + \]

\[ \left[ \left( \frac{b}{\theta_D^5} \right) J_5 \left( \frac{\theta_D}{T} \right) - \left( \frac{a}{T_{sf}^5} \right) J_5 \left( \frac{T_{sf}}{T} \right) \right] T^5. \tag{6.11} \]

It is evident from Eqn. (6.11) that the electron-spin fluctuations interactions not only give rise to the quadratic temperature dependence of resistivity at low temperatures but also attenuates the usual Bloch-Gruneisen \( T^5 \) term. Furthermore, the coefficient of the \( T^5 \) term may be even negative if the contribution arises from the electron-spin fluctuations scatterings is greater than that from the electron-phonon scatterings. Thus, we find that all the characteristic features observed in the temperature dependence of resistivity of the Ti\(_{0.4}\)V\(_{0.6}\) and Ti\(_{0.6}\)V\(_{0.4}\) alloys at low temperatures can be explained by considering the presence of spin fluctuations in these alloys. The coefficient \( A \) of the \( T^2 \) term in the temperature dependence of resistivity is found to decrease with the increase in \( x \), which indicates that the role of spin fluctuations diminishes with the increase in Ti concentration in the Ti-V alloys. The tem-
perature at which resistivity exhibits a deviation from the linear temperature
dependence at high temperature regime can be taken as the characteristic
spin-fluctuation temperature $T_{sf}$. The values of $T_{sf}$ for the Ti$_x$V$_{1-x}$ alloys
with compositions $x = 0.4$ and 0.6 are given in Table 6.2. It then seems
reasonable to assume that the observed deviation of the experimental $C(T)$
data from the curve fitted by considering the contributions from electrons
and the lattice may be due to increasing importance of spin fluctuations in
these Ti-V alloys at temperatures below $T_{sf}$, and therefore, the temperature
for observing such deviation can be considered as $T_{sf}$. Accordingly, we have
estimated $T_{sf}$ values for the Ti$_x$V$_{1-x}$ alloys with $x = 0.4$ and 0.6 from the
heat capacity data, which are found to be very similar to those obtained from
the resistivity data. On the other hand, Frings and Franse had shown that
the $T_{sf}$ may be identified from the $\chi(T)$ data as the temperature at which
the second derivative of $\chi$ with respect to temperature goes to zero [191]. For
an example, the second derivative of $\chi$ goes to zero at temperature $T \sim 120$
K for the Ti$_{0.6}$V$_{0.4}$ alloy, which is slightly higher than the $T_{sf}$ value obtained
from the temperature dependence of resistivity and heat capacity data.

The temperature coefficient of resistivity (TCR) $\alpha (= d\rho/dT)$ is negative
for the Ti$_{0.7}$V$_{0.3}$ and Ti$_{0.8}$V$_{0.2}$ alloys over a considerably large temperature
range. These results are consistent with the previous studies, where a nega-
tive TCR was reported for the Ti$_x$V$_{1-x}$ alloys having concentrations in the
range $0.6 < x < 0.85$ [42-44]. For the Ti$_{0.7}$V$_{0.3}$ alloy, the resistivity initially
decreases as the temperature is decreased from 300 K, and reaches to the
minimum value near to 210 K. Resistivity then starts to increase with further lowering of the temperature from 210 K down to 65 K. For temperatures below 65 K, $\rho(T)$ curve exhibits another weak minimum at temperature close to 30 K, which is visible in the inset of the Fig. 6.5(b). The main panel of Fig. 6.5(b) shows the temperature dependence of resistivity for the Ti$_{0.7}$V$_{0.3}$ alloy, where temperature is plotted in log scale. In the temperature range 70-170 K, $\rho(T)$ curve is linear with a negative slope which indicates a $-\ln T$ dependence of resistivity of this alloy in the said temperature regime. The $-\ln T$ dependence of resistivity is known to arise due to either the spin-Kondo effect [192] or TLS (Two-level-system)-Kondo effect [72]. The spin-Kondo effect arises due to the screening of the magnetic moments by conduction electrons in very dilute magnetic alloys, and the effect is known to depend strongly on the applied magnetic field [72]. However, in the present case, it is observed that the $\rho(T)$ curve of the Ti$_{0.7}$V$_{0.3}$ alloy remains unaffected by the application of magnetic fields. This is shown in the inset of Fig. 6.5(b), where the temperature dependence of resistivity measured in zero and 5 T applied magnetic fields is shown for this alloy in the temperature range 10-300 K. On the basis of this observation we argue that the observed $-\ln T$ dependence of resistivity of the Ti$_{0.7}$V$_{0.3}$ alloy cannot be of magnetic origin. The observed behaviour of $\rho(T)$ is therefore attributed to the TLS-Kondo effect. The TLS-Kondo model has been used previously in order to explain the negative TCR of the Ti-V [47] as well as Nb-Ti alloys [46, 47, 193]. The previous studies suggest that the TLS-Kondo effect is related to the formation
of the submicroscopic $\omega$ phase precipitations within the main $\beta$ phase matrix of these disordered transition metal alloys. The $\omega$ phase precipitations are known to be formed due the lattice instability associated with the main $\beta$ phase matrix. In fact, the TLS-Kondo effect becomes the dominant mechanism for the electron scattering process in transition metal alloys, which are at the verge of the $\beta$ to $\omega$ structural phase transformation [194]. Previously, C. C. Tsuei had suggested that the formation of the submicroscopic $\omega$ phase can lead to structural indeterminacy in the atomic arrangements in these disordered transition metal alloys [194]. Consequently, there exist a number of local atomic arrangements which are energetically equivalent. As a possible consequence of this fact, a significant number of atoms or group of atoms can tunnel between the states of equivalent energies, i.e., the atoms or group of atoms constitute the two-level-systems (TLS) [194]. The TLS model due to Cochrane et al. [72] explains that the two-level state can scatter the conduction electrons in a way analogous to the spin-Kondo type exchange interactions giving rise to the negative TCR with a characteristic $-\ln T$ dependence of resistivity in many disordered materials. The present Ti$_{0.7}$V$_{0.3}$ alloy contains $\omega$ phase within the main $\beta$ phase matrix of this alloy, which clearly indicates the instability of the main $\beta$ phase matrix of this alloy. In such case, the exhibition of the TLS-Kondo effect is indeed expected.

We have already stated above that a weak dip-like feature is observed in the $\rho(T)$ curve of the Ti$_{0.7}$V$_{0.3}$ alloy at temperatures below 65 K. Such a resistivity dip indicates the interplay of at least two kinds of resistivity con-
tributions with opposite signs of TCR, e.g., a negative TCR due to the TLS-Kondo effect, and a positive TCR that may arise due to various mechanisms including electron-phonon, electron-magnon, and the electron-spin fluctuations scattering. However, the phononic contribution is generally observed to be negligible in materials where the TLS-Kondo scattering is a dominant electron scattering process [194]. Moreover, the role of the electron-phonon scattering is expected to be much reduced at low temperatures. We have already ruled out the presence of any appreciable magnetic impurities in the present Ti-V alloys. Hence, the possibility of a contribution towards the positive TCR due to the electron-magnon scattering can also be ruled out for the Ti$_{0.7}$V$_{0.3}$ alloy. However, a quadratic temperature dependence of resistivity is observed at low temperatures in the case of Ti$_{0.4}$V$_{0.6}$ and Ti$_{0.6}$V$_{0.4}$ alloys, which has been inferred to arise due to the scattering of the conduction electrons by spin fluctuations. Hence, we infer that the dip-like feature observed in the $\rho(T)$ curve of the Ti$_{0.7}$V$_{0.3}$ alloy at low temperatures arises due to the contributions from the TLS-Kondo scattering mechanism and most probably the electron-spin fluctuations scattering mechanism, which becomes effective only below the spin fluctuation temperature $T_{sf}$. In such a case, we can estimate $T_{sf}$ for this alloy by finding the temperature below which resistivity exhibits a deviation from showing a $-\ln T$ behaviour at low temperatures. A value of $T_{sf}\sim65$ K is obtained for the Ti$_{0.7}$V$_{0.3}$ alloy, which is lower as compared to the $T_{sf}$ of both Ti$_{0.4}$V$_{0.6}$ and Ti$_{0.6}$V$_{0.4}$ alloys. Moreover, we observe that the characteristic spin fluctuation temperature $T_{sf}$ gradually decreases
with the increase in Ti concentration in the Ti-V alloys. This result again implies that the role of spin fluctuations in the Ti-V alloys becomes suppressed as the Ti concentration is increased in these alloys.

Figure 6.6: (a) Resistivity versus $\sqrt{T}$ plot for the Ti$_{0.8}$V$_{0.2}$ alloy to show the $-\sqrt{T}$ dependence of resistivity at low temperatures (16-50 K). Its inset show the plot of the temperature dependence of resistivity of the Ti$_{0.8}$V$_{0.2}$ alloy, where temperature is plotted in log scale. (b) The magneto-resistance of the Ti$_{0.8}$V$_{0.2}$ alloy at various constant temperatures.

The TCR is negative for the Ti$_{0.8}$V$_{0.2}$ alloy in the entire temperature range of the present measurements [Fig. 6.4(d)]. The main panel of Fig. 6.6(a) shows the plot of resistivity against $\sqrt{T}$ in the temperature range 15-60 K for the Ti$_{0.8}$V$_{0.2}$ alloy. The observed linearity of this plot with a negative slope suggests that the resistivity in this alloy varies with temperature as $\rho(T) \propto -\sqrt{T}$ in the said temperature range. At higher temperatures, $\rho(T)$ curve deviates from showing the $-\sqrt{T}$ behaviour, and follows the $-\ln T$ dependence for temperatures above 200 K [shown in the inset of Fig. 6.6(a)]. In Fig. 6.6(b), we show the field dependence of magneto-resistance.
of the Ti$_{0.8}$V$_{0.2}$ alloy at few selected constant temperatures. Superconducting fluctuation induced conductivity gives rise to the strong positive magneto-resistance in this alloy at temperatures up to about 15 K (refer to chapter 5). For still higher temperatures, a weak negative magneto-resistance is observed for this alloy. However, the magneto-resistance becomes vanishingly small at temperatures $T$=80 K and above (these data are not shown here). The negative magneto-resistance along with the $-\sqrt{T}$ dependence of resistivity implies that the electron conduction mechanism in the Ti$_{0.8}$V$_{0.2}$ alloy is governed by the weak-localization effect [195]. In fact, weak-localization effect is known to become important particularly in highly disordered materials. Among all the present Ti-V alloys, Ti$_{0.8}$V$_{0.2}$ alloy has the highest value of normal state resistivity. This indicates that the degree of disorder is the highest in the Ti$_{0.8}$V$_{0.2}$ alloy among the present T-V alloys. The mean free path for the conduction electrons $\ell_e$ is estimated for this alloy using the free electron model, which comes out to be almost comparable to the inter-atomic distance. Such a small value of $\ell_e$ is generally considered to be a pre-requisite for observing the weak-localization effect. However, the weak-localization is known to be a low-temperature phenomenon, and generally becomes less significant at higher temperatures. Consequently, the TLS-Kondo effect becomes the dominant electron scattering mechanism to govern the electrical resistivity of the Ti$_{0.8}$V$_{0.2}$ alloy at high temperature regime. This is indicated by the observed $-lnT$ dependence of resistivity and almost zero magneto-resistance of this alloy at high temperature regime.
Figure 6.7: Kadowaki-Woods scaling for the Ti$_{0.4}$V$_{0.6}$ (black solid circle) and Ti$_{0.6}$V$_{0.4}$ (red solid square) alloys along with various heavy Fermion and spin fluctuation systems. The solid line represents the function $A/\gamma^2 = 1.0 \times 10^{-4} \mu\Omega\cdot\text{cm}(\text{mole/mJ})^2$.

6.2.4 Validity of the Kadowaki-Woods scaling relation for the Ti-V alloys

For the heavy Fermion and Spin fluctuation systems, the coefficient $A$ of the quadratic term in the temperature dependence of resistivity and the Sommerfeld coefficient of the electronic heat capacity $\gamma$ scale according to the Kadowaki-Woods relation [180] given as: $A/\gamma^2 = 1.0 \times 10^{-4} \mu\Omega\cdot\text{cm}^2(\text{mole/mJ})^2$.

The plots of the coefficient $A$ against $\gamma$ for the Ti$_x$V$_{1-x}$ alloys with compositions $x = 0.4$ and 0.6 along with various heavy Fermion and spin fluctuation systems are shown in Fig. 6.7 in log-log scales. The Kadowaki-Woods scaling relation is found to be valid for both these Ti-V alloys, which further supports the presence of spin fluctuations in the Ti-V alloys.
6.2.5 Suppression of $T_C$ due to spin fluctuations in the Ti-V alloys

The influence of spin fluctuations on the suppression of $T_C$ of a superconductor is known to be non-trivial. The strong suppression of $T_C$ in the elemental superconductors such as V and Nb [92, 196, 197], and the absence of superconductivity in Pd and Pt [89, 198] are known to be due to the strong presence of spin fluctuations in these materials. We therefore revisit the problem of $T_C$ in the Ti-V alloys with the inclusion of the effect of spin fluctuations in these alloys. In such case, $T_C$ can be estimated using the modified McMillan formula which takes into account the effect of spin fluctuations, and is given by [199]

$$T_C = \frac{\theta_D}{1.45} \exp \left[ -\frac{1.04(1 + \lambda_{eff})}{\lambda_{eff} - \mu^*_{eff}(1 + 0.62\lambda_{eff})} \right]. \quad (6.12)$$

In the above expression, $\lambda_{eff}$ and $\mu^*_{eff}$ are the normalized parameters which are expressed as $\lambda_{eff} = \lambda_{ep}/(1 + \lambda_{sf})$ and $\mu^*_{eff} = (\mu^* + \lambda_{sf})/(1 + \lambda_{sf})$, where $\lambda_{sf}$ being the electron-spin fluctuations coupling constant [199]. In the previous chapter as well as in Sec. 6.2 of the present chapter, the considerations for the spin fluctuations were not taken into account for the estimation of $T_C$ using McMillan formula. Considering the additional re-normalization due to the electron-spin fluctuation interactions the Sommerfeld coefficient of the electronic heat capacity can be expressed as

$$\gamma = \frac{1}{3} \pi^2 k_B^2 N(0)(1 + \lambda_{ep} + \lambda_{sf}). \quad (6.13)$$
Using the value of $N(0)$ obtained from the band structure calculations and the experimentally measured $T_C$, $\theta_D$ and $\gamma$ values in Eqns. (6.12) and (6.13), we can estimate the values of $\lambda_{ep}$ and $\lambda_{sf}$ without any ambiguity. The values of $\lambda_{ep}$ and $\lambda_{sf}$ thus estimated for the present $\text{Ti}_x\text{V}_{1-x}$ alloys are given in Table 6.3. We observe that in the $\text{Ti}_x\text{V}_{1-x}$ alloys, both $\lambda_{ep}$ and $\lambda_{sf}$ increase with the decrease in the Ti concentration $x$. This implies that the initial increase in the experimental $T_C$ with decreasing $x$ down to 0.4 is due to the increase in electron-phonon coupling constant. With further decrease in $x$ below 0.4, the experimental $T_C$ decreases and reaches a value of about 5.4 K for pure V [see Fig. 1.13 (a)]. For the $\beta$ phase $\text{Ti}_x\text{V}_{1-x}$ alloy system, the residual resistivity $\rho_0$ decreases progressively as $x$ is decreased [70]. Accordingly, $d\rho/dT$ is expected to increase progressively as $x$ is decreased in these $\beta$ phase $\text{Ti}_x\text{V}_{1-x}$ alloys. Since $\lambda_{ep} \propto d\rho/dT$ [196], then $\lambda_{ep}$ is also expected to increase with the decrease in $x$ in the $\text{Ti}_x\text{V}_{1-x}$ alloys. For the present Ti-V alloys, the observed trend of the variation of $\lambda_{ep}$ with the alloy concentration is consistent with this prediction. Moreover, a relatively higher value of $\lambda_{ep} \sim 1.3$ for the elemental V [91, 92] is also commensurate with the above prediction. Since both $\lambda_{ep}$ and $\theta_D$ [see Fig. 1.12(a)] increases with the decrease in Ti concentration $x$ in the $\text{Ti}_x\text{V}_{1-x}$ alloys with $x \leq 0.4$, then if we disregard the influences of the spin fluctuations, $T_C$ should increase as $x$ is decreased in these Ti-V alloys. In spite of this, the experimental $T_C$ is found to decrease as $x$ is lowered below 0.4. We attribute this to the much stronger influence of the spin fluctuations on $T_C$ of the V-rich Ti-V alloys.
Table 6.3: The electron-phonon coupling constant $\lambda_{ep}$ and the electron-spin fluctuation coupling constant $\lambda_{sf}$ for the Ti-V alloys.

<table>
<thead>
<tr>
<th></th>
<th>Ti$<em>{0.4}$V$</em>{0.6}$</th>
<th>Ti$<em>{0.6}$V$</em>{0.4}$</th>
<th>Ti$<em>{0.7}$V$</em>{0.3}$</th>
<th>Ti$<em>{0.8}$V$</em>{0.2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{sf}$</td>
<td>0.12±0.001</td>
<td>0.042±0.002</td>
<td>0.04±0.002</td>
<td>0</td>
</tr>
<tr>
<td>$\lambda_{ep}$</td>
<td>1.068±0.005</td>
<td>0.86±0.005</td>
<td>0.84±0.002</td>
<td>0.59±0.001</td>
</tr>
</tbody>
</table>

6.3 Summary and conclusions

We have studied the normal state properties of the Ti-V alloys by measuring the temperature dependence of heat capacity, dc magnetic susceptibility and electrical resistivity. We have estimated the Stoner enhancement factor $S$ and also test the validity of the Kadowaki-Woods scaling relation in order to ascertain the presence of spin fluctuations in the Ti-V alloys. The outcome of the study on the normal states properties of the Ti-V alloys is then used to explain the observed disagreement of the experimental $T_C$ with the theory. The following conclusions are made in this chapter.

(i) The presence of spin fluctuations in the Ti-V alloys rich enough in V concentration is inferred from: (a) the observed deviation of the experimental heat capacity data from the fitted curve based on the relation $C(T) = \gamma T + C_L(T)$ at low temperatures, where $C_L(T)$ represents the Debye lattice heat capacity; (b) the non-linearity and the negative
curvature in $C/T$ versus $T^2$ plots at low temperatures; (c) $-T^2\ln(T)$ dependence of the dc magnetic susceptibility; (d) the enhancement of the Stoner factor $S$; (e) a higher value of the Wilson’s coefficient $R_W$ than unity; (f) $T^2$ dependence of resistivity at low temperatures; and (g) the validity of the Kadowaki-Woods scaling relation. The role of spin fluctuations is diminished with the increase in Ti concentration in the Ti-V alloys.

(ii) The presence of spin fluctuations gives rise to a strong suppression of $T_C$ in the Ti$_x$V$_{1-x}$ alloys having concentrations $x = 0.4, 0.6$ and 0.7.

(iii) Similar to $\lambda_{ep}$ and $\theta_D$, $\lambda_{sf}$ is also found to increase with the decrease in Ti concentration $x$ in the Ti$_x$V$_{1-x}$ alloys. We suggest that the initial increasing trend of $T_C$ of the Ti$_x$V$_{1-x}$ alloys with the decrease in $x$ down to 0.4 is due to the increase of both $\lambda_{ep}$ and $\theta_D$ with the decrease in $x$. In spite of increase of both $\lambda_{ep}$ and $\theta_D$ with increasing $x$ in the Ti$_x$V$_{1-x}$ alloys, $T_C$ exhibit a decreasing trend with further lowering of $x$ below 0.4 and reaches a value of about 5.4 K for elemental V. We have attributed this to the increasing role of the spin fluctuations with the decrease in $x$ in the V rich end of the Ti-V alloy system.