High Temperature NMR Study of $^{51}$V and $^{195}$Pt in the V$_3$Pt Compound

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Measurements of both the $^{51}$V and $^{195}$Pt Knight shift in the V$_3$Pt compound are reported for temperatures ranging from 300 K to about 1300 K. The temperature coefficients of the Knight shift and the NMR linewidth have been determined. An interpretation of the observations is given in the frame of a model which is based on the temperature dependence of the core polarization contribution to the total Knight shift.

1. Introduction

Extensive investigations of nuclear magnetic resonance properties of A15 type compounds have been made since correlations between these properties and the superconductivity in binary Vanadium A15 type compounds have been found [1–3]. As reported in [1], A15 type compounds with the highest superconducting transition temperature $T_c$ show the greatest temperature coefficient of the Vanadium Knight shift $K(51V)$ in the normal state. The mechanisms responsible for the high $T_c$ in these compounds have been mainly attributed to a fine structure in the density of electronic states, with a high peak near the Fermi energy $E_F$ [2, 4], or to a phonon softening related to lattice structural instability [5]. A deeper understanding of such a complex phenomenon could be reached on the basis of a systematic investigation of the electronic and atomic structure of these compounds.

We measured the $^{51}$V and $^{195}$Pt Knight shift in the V$_3$Pt compound over an extended temperature range in order to obtain insight into the electronic structure and the temperature parametric behavior of the different interactions responsible for the hyperfine field at the position of the nucleus.

2. Experimental

For the measurements we used a cw spectrometer combined with a usual computer as a signal averager. A derivative signal of the absorption mode was detected using a magnetic field sweep and a modulation of 39 Hz. The stability of the external magnetic field has been controlled via proton NMR. The main difficulties associated with high temperature Knight shift measurements are firstly the avoidance of disturbing magnetic fields at the position of the NMR sample caused by the heating element current or by temperature dependent magnetization effects; and secondly the avoidance of large temperature gradients over the NMR sample volume. We used a high temperature furnace with a maximum disturbing magnetic field $B_d = 0.4$ mG and a temperature gradient at the center of the heating element of about 2 °C • cm$^{-1}$ at 1000 K. Details of the high temperature NMR spectrometer and sample preparation are presented elsewhere [6, 7].

3. Experimental results

The temperature dependence of the Vanadium Knight shift $K(51V)$ in V$_3$Pt is shown in Figure 1a. From these first results for $K(51V)$ in V$_3$Pt in the high temperature range 300 K – 1300 K we determined the average temperature coefficient $x_1$ as

$$x_1 = (2.5 \pm 0.5) \times 10^{-5} \%/K.$$  

In [1] the value for $x$ in the low temperature range between $T_c = 2.8$ K and 300 K had been given as

$$x_2 = (9 \pm 1) \times 10^{-5} \%/K.$$  

For the $^{51}$V NMR linewidth $\Delta B$ in V$_3$Pt we found the almost temperature independent value: $\Delta B = (9.2 \pm 0.4)$ G. For the determination of $K(51V)$ in V$_3$Pt we used V$_3$(SO$_4$)$_2$3 as a reference sample.

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The experimental results of the present work referring to \( K(^{51}\text{V}) \) in \( \text{V}_3\text{Pt} \) show in connection with our previous ones for \( K(^{51}\text{V}) \) in \( \text{V}_3\text{Si}, [3] \) and \( \text{V}_3\text{Ga} \) [9] that the correlation between the superconducting transition temperature \( T_c \) and the temperature coefficient of \( K(^{51}\text{V}) \) in these compounds also exists in the high temperature range. In the low temperature range (\( T_c < 300 \text{ K} \)) it has been found, [1], that the \( \text{V}_3\text{X} \) compounds (\( \text{X} = \text{Si}, \text{Ga}, \text{Pt} \)) with the highest \( T_c \) show the largest temperature coefficient of \( K(^{51}\text{V}) \) in the normal state. Table 1 presents the values of the average temperature coefficient \( z \) of \( K(^{51}\text{V}) \) for the different compounds, taken from our results and the corresponding \( T_c \) values in [1]. An interpretation of the temperature dependence of \( K(^{51}\text{V}) \) in \( \text{V}_3\text{Pt} \) is given in terms of a model which implies that the temperature dependence of the Knight shift is associated only with the d-spin contribution to the total (measured) Knight shift. This model has been used earlier to explain Knight shift results in transition metal systems [1–3, 10]. The measured Knight shift \( K \) is separated into a) the \( K_s \) contribution associated with s-spin electrons, b) the \( K_d(T) \) contribution associated with d-spin electrons (this part of \( K \) is assumed to be temperature dependent), and c) \( K_{\text{orb}} \), the orbital contribution. Other terms contributing to \( K \) are negligibly small [10, 11]:

\[
K(T) = K_s + K_d(T) + K_{\text{orb}} .
\]

If there is a proportionality between the different contributions of \( K \) and its corresponding susceptibilities, (1) can be written in the form

\[
K(T) = A_s z_s + A_d z_d(T) + A_{\text{orb}} z_{\text{orb}}
\]

with

\[
z(T) = z_s + z_d(T) + z_{\text{orb}} .
\]

Table 1. The average temperature coefficient \( z \) of the Vanadium Knight shift \( K(^{51}\text{V}) \) in the different compounds for the range 300 K–1300 K (our results). The superconducting transition temperature \( T_c \) for the compounds has been taken from reference [1].

<table>
<thead>
<tr>
<th>Compound</th>
<th>( V_3\text{Si} )</th>
<th>( V_3\text{Ga} )</th>
<th>( V_3\text{Pt} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( z ) (10^{-5} % /K)</td>
<td>4.2 ± 0.5</td>
<td>5.5 ± 0.5</td>
<td>2.5 ± 0.5</td>
</tr>
<tr>
<td>( T_c ) (K)</td>
<td>17.1</td>
<td>16.5</td>
<td>2.8</td>
</tr>
</tbody>
</table>
where $\chi$ is the measured total susceptibility (the diamagnetic part has been neglected). In this concept $A_0$ is assumed to be negative \[12.3\]. If $\chi_d$ decreases with increasing temperature (this is a reasonable assumption), the magnitude of the negative term in (2) becomes smaller and consequently the total (measured) Knight shift $K(T)$ increases. This is what we found experimentally as shown in Figure 1a.

As shown in Fig. 1b, $K(^{195}\text{Pt})$ in $\text{V}_3\text{Pt}$ is negative and decreases absolutely with increasing temperature. This behavior can also be interpreted in the frame of the above model. The d-spin electrons via an exchange polarization of inner s-shell electrons cause at the position of the $^{195}\text{Pt}$ nucleus a dominant negative Knight shift. With increasing temperature the d-spin susceptibility $\chi_d$ decreases absolutely and therefore the absolute value of the Knight shift decreases, too.

As has been discussed above, the same mechanism is responsible for the temperature behavior of both $K(^{51}\text{V})$ and $K(^{195}\text{Pt})$ in $\text{V}_3\text{Pt}$. If $K(^{51}\text{V})$ and $K(^{195}\text{Pt})$ are both linear functions of the susceptibility, they must also show a linear relation to each other. In Fig. 2 $K(^{51}\text{V})$ has been plotted versus $K(^{195}\text{Pt})$ with the temperature as an implicit parameter. Within the experimental error there is a linear relation between $K(^{51}\text{V})$ and $K(^{195}\text{Pt})$ in $\text{V}_3\text{Pt}$. It could be of particular interest to relate $\text{V}_3\text{Pt}$ high temperature experimental results for Knight shift with those for susceptibility of the same compound. But unfortunately no high temperature susceptibility results have been found in the literature.

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