High Temperature NMR Study of ^{51}V and ^{195}Pt in the V_3Pt Compound

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Measurements of both the ^{51}V and ^{195}Pt Knight shift in the V_3Pt 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 $K(^{51}V)$ 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_3Pt 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 $2\,^\circ C \cdot cm^{-1}$ at 1000 K. Details of the high temperature NMR spectrometer and sample preparation are presented elsewhere [6, 7].

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3. Experimental results

The temperature dependence of the Vanadium Knight shift $K(^{51}V)$ in V_3Pt is shown in Figure 1a. From these first results for $K(^{51}V)$ in V_3Pt in the high temperature range 300 K – 1300 K we determined the average temperature coefficient α_1 as

$$\alpha_1 = (2.5 \pm 0.5) \cdot 10^{-5}\,\%/K\,.$$

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

$$\alpha_2 = (9 \pm 1) \cdot 10^{-5}\,\%/K\,.$$

For the ^{51}V NMR linewidth ΔB in V_3Pt we found the almost temperature independent value: $\Delta B = (9.2 \pm 0.4)$ G. For the determination of $K(^{51}V)$ in V_3Pt we used $V_3(SO_4)_3$ as a reference sample.

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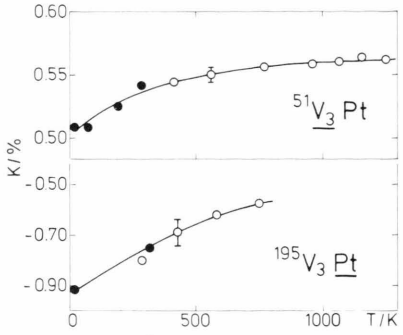

Fig. 1 a) The ^{51}V Knight shift $K(^{51}V)$ in the V_3Pt compound. (Open circles: present work, closed circles: reference [1].) – b) The ^{195}Pt Knight shift $K(^{195}Pt)$ in the V_3Pt compound. (Open circles: present work, closed circles: reference [1].)

Figure 1 b shows the temperature dependence of the ^{195}Pt Knight shift in V_3Pt. The NMR signal of ^{195}Pt in V_3Pt could only be observed up to 750 K. For higher temperatures the signal-to-noise ratio was extremely weak so that a very long measuring time would have been needed in order to get useful data. Difficulties connected with the NMR signal of ^{195}Pt in V_3Pt at low temperatures have been mentioned also in [8]. It should be emphaziued that for the determination of $K(^{195}Pt)$ in V_3Pt the choice of the reference sample is of particular importance. In this work we used H_2PtCl_6 as a reference sample and found $K(^{195}Pt)$ to remain negative over the entire measuring range (Figure 1 b). If the association H_2PtJ_6 were used as a reference sample for $K(^{195}Pt)$ in V_3Pt, $K(^{195}Pt)$ would change from negative to positive values at 340 K. According to our results the temperature coefficient of $K(^{195}Pt)$ in V_3Pt is not constant in the range from 300 K to 750 K. However, an average slope from our high temperature results and the low temperature results in [1], which are in good agreement with ours, yields at 300 K a temperature coefficient for $K(^{195}Pt)$ with the value

$$\beta = (52 \pm 3) \cdot 10^{-5}\,\%/\mathrm{K}\,.$$

The NMR linewidth ΔB of ^{195}Pt in V_3Pt has been found to amount to

$$\Delta B\,(^{195}Pt) = (10 \pm 2)\ \mathrm{G}\,.$$

Within the experimental error it is temperature independent.

4. Discussion

The experimental results of the present work referring to $K(^{51}V)$ in V_3Pt show in connection with our previous ones for $K(^{51}V)$ in V_3Si, [3] and V_3Ga [9] that the correlation between the superconducting transition temperature T_c and the temperature coefficient of $K(^{51}V)$ in these compounds also exists in the high temperature range. In the low temperature range ($T_c - 300$ K) it has been found, [1], that the V_3X compounds (X = Si, Ga, Pt) with the highest T_c show the largest temperature coefficient of $K(^{51}V)$ in the normal state. Table 1 presents the values of the average temperature coefficient α of $K(^{51}V)$ for the different compounds, taken from our results and the corresponding T_c values in [1]. An interpretation of the temperature dependence of $K(^{51}V)$ in V_3Pt 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_{orb}, the orbital contribution. Other terms contributing to K are negligibly small [10, 11]:

$$K(T) = K_s + K_d(T) + K_{orb}\,. \tag{1}$$

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

$$K(T) = A_s \chi_s + A_d \chi_d(T) + A_{orb} \chi_{orb} \tag{2}$$

with

$$\chi(T) = \chi_s + \chi_d(T) + \chi_{orb}\,, \tag{3}$$

Table 1. The average temperature coefficient α of the Vanadium Knight shift $K(^{51}V)$ 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].

Compound	V_3Si	V_3Ga	V_3Pt
$\alpha\,(10^{-5}\,\%/\mathrm{K})$	4.2 ± 0.5	5.5 ± 0.5	2.5 ± 0.5
T_c(K)	17.1	16.5	2.8

where χ is the measured total susceptibility (the diamagnetic part has been neglected). In this concept A_d is assumed to be negative [12, 3]. If χ_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 1 a.

As shown in Fig. 1 b, $K(^{195}Pt)$ in V_3Pt 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}Pt nucleus a dominant negative Knight shift. With increasing temperature the d-spin susceptibility χ_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 $K(^{51}V)$ and $K(^{195}Pt)$ in V_3Pt. If $K(^{51}V)$ and $K(^{195}Pt)$ are both linear functions of the susceptibility, they must also show a linear relation to each other. In Fig. 2 $K(^{51}V)$ has been plotted versus

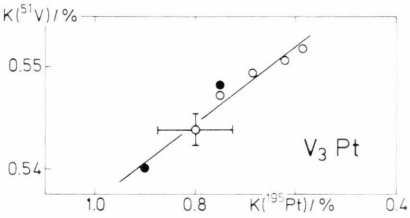

Fig. 2. The ^{51}V Knight shift $K(^{51}V)$ against the ^{195}Pt Knight shift $K(^{195}Pt)$ in the V_3Pt compound with the temperature as an implicit parameter. (Open circles: present work, closed circles: reference [1].)

$K(^{195}Pt)$ with the temperature as an implicit parameter. Within the experimental error there is a linear relation between $K(^{51}V)$ and $K(^{195}Pt)$ in V_3Pt. It could be of particular interest to relate V_3Pt 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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