

Nuclear Magnetic Resonance of ^{51}V in V_3Si and VSi_2 at High Temperatures

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The Knight shift of the ^{51}V resonance has been measured as a function of temperature in polycrystalline V_3Si and VSi_2 samples. For the V_3Si system the measurements have been extended to the temperature range from 400 K up to 1250 K, whereas for VSi_2 the first NMR measurements at all have been carried out, covering the range 300 to 1250 K. The observed ^{51}V Knight shift in VSi_2 is negative ($K_{^{51}\text{V}}(T = 272 \text{ K}) = -0.15\%$) and tends to zero with increasing temperature.

1. Introduction

The electronic properties of intermetallic A_3B compounds with an A-15 or β -tungsten structure have been the subject of many investigations, e.g. [1], [2], [3]. The main reason for this focus of research is the fact that some of these compounds have considerably high superconduction transition temperatures T_c . As it is known, the highest experimental transition temperatures are about 23 K. It is of particular interest to ask which mechanism or mechanisms are responsible for this T_c limit. Previous experimental investigations by Blumberg et al. [4] reveal striking correlations between the NMR properties and the superconduction transition temperature of Vanadium intermetallic compounds such as V_3Si , V_3Ga , V_3Ge . For example, Blumberg et al. found that the compounds with the highest T_c show the greatest variation of the ^{51}V Knight shift with temperature in the normal state. Therefore it is interesting to carry out high temperature investigations which may increase our insight into the electronic structure and the different interactions in these materials.

We measured the ^{51}V Knight shift in the extended temperature range from 400 K up to 1250 K. For further information about the effects on the hyperfine fields at the Vanadium nucleus caused by different atomic environments of silicon atoms, we measured the temperature dependence of the ^{51}V Knight shift in VSi_2 compound.

2. Experimental

The samples of polycrystalline V_3Si were prepared by standard arc-furnace techniques. We used bulk materials with a purity of 99.9999% for Si and 99.995% for V (Ventron-Alfa products). The samples were crushed and sieved to get particles with a maximum diameter of 50 μm .

Electrical insulation was achieved by mixing the sample particles with an approximately equal volume of annealed Al_2O_3 powder. Before sealing the quartz tubes containing the so-prepared material, the sample was heated under vacuum to several hundred degrees Celsius to drive off adsorbed water.

The experiments were carried out in a cw-NMR spectrometer using a modified Pound-Knight-Watkins NMR detector which has been described elsewhere (Ploumbidis [5]).

3. Experimental Results

The measured temperature dependence of the ^{51}V Knight shift $K_{^{51}\text{V}}$ in V_3Si compound is shown in Figure 1. Previous results concerning $K_{^{51}\text{V}}$ exist only for temperatures up to 500 K. Figure 1 shows that they agree with our results within the experimental error.

$K_{^{51}\text{V}}$ has approximately the same magnitude in V_3Si as in pure V and does not show any appreciable temperature dependence in the range from 300 to 1250 K, as is also the case in the pure V metal.

The temperature coefficient for $K_{^{51}\text{V}}$ in V_3Si is found to be

$$\alpha = dK_{^{51}\text{V}}/dT = 10.5 \cdot 10^{-5} \% \cdot \text{K}^{-1}.$$

Figure 2 shows the first experimental results for

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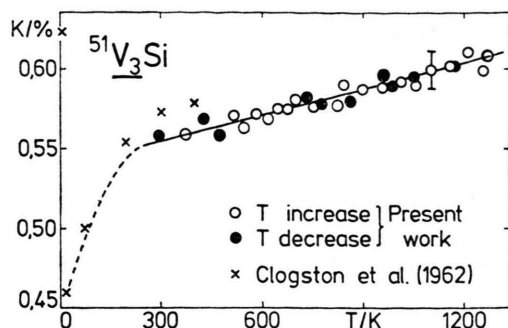


Fig. 1. The ^{51}V Knight shift K in V_3Si as a function of temperature.

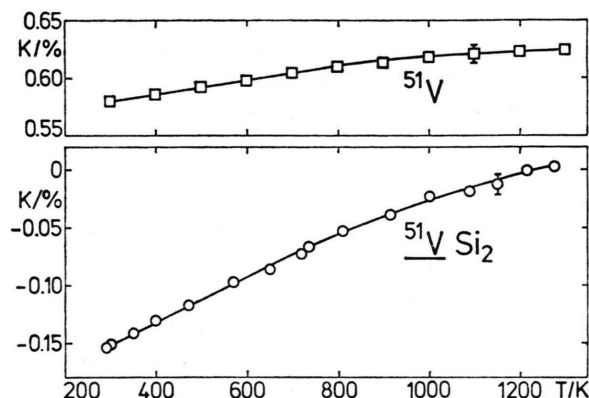


Fig. 2. The ^{51}V Knight shift K in pure V metal (upper part of the Figure) and in the VSi_2 compound as a function of temperature.

$K_{^{51}\text{V}}$ in VSi_2 . The temperature dependence of $K_{^{51}\text{V}}$ in this compound is also weak, but its values are negative and tend to zero with increasing temperature.

The linewidths ΔB of the ^{51}V resonance in V_3Si and in VSi_2 are almost temperature-independent over the range (300 ... 1250) K. We find the average values

$$\Delta B_1 = 11.9 \pm 0.8 \text{ G for } \text{V}_3\text{Si},$$

$$\Delta B_2 = 9.5 \pm 0.6 \text{ G for } \text{VSi}_2.$$

4. Discussion

In the frame of the present work we measured the ^{51}V Knight shift $K_{^{51}\text{V}}$ also in pure metal in order to get a reasonable comparison for the $K_{^{51}\text{V}}$ values in V_3Si and in VSi_2 compounds. The results for $K_{^{51}\text{V}}$ in pure Vanadium are shown in the upper part of Figure 2. Existing data in the literature for $K_{^{51}\text{V}}$ in

pure V at high temperatures, given by Chabre and Segransan [6], agree very well with our results. The $K_{^{51}\text{V}}$ values in V_3Si lie only about 6% below those in pure Vanadium, over the entire temperature range.

An interpretation of the temperature dependence of $K_{^{51}\text{V}}$ in V_3Si may be given in terms of a model which has been used earlier to explain experimental Knight shift results in transition pure metals and alloys, Clogston and Jaccarino [7, 8]. In this model, the temperature dependence of the Knight shift is assumed to be associated only with the d-spin contribution. The measured Knight shift K is separated into the d-spin temperature-dependent part, $K_d(T)$, and the temperature-independent parts as follows:

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

where K_s and K_{orb} are the s-electron and orbital contributions to the total Knight shift, respectively. The diamagnetic term and the higher order terms in (1) are negligibly small, [8, 9].

If the hyperfine interaction A is constant, then the different contributions in (1) are proportional to the corresponding susceptibilities, and we can write

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

$$\chi(T) = \chi_s + \chi_d(T) + \chi_{\text{orb}}; \quad (3)$$

χ_s , χ_d and χ_{orb} are the s-spin, d-spin and orbital susceptibilities, respectively. A_s , A_d and A_{orb} are the corresponding hyperfine fields, and χ is the measured magnetic susceptibility, in which diamagnetic contributions have been neglected.

It is a well-known fact that half-filled shells of p, d and f electrons have non-zero hyperfine fields. These fields are — among other mechanisms — due to the core polarization. Estimates of the hyperfine fields associated with the core polarization are based on experimental data and on exchange polarization calculations in the frame of the Hartree-Fock theory, Watson and Freeman [10]. The core polarization hyperfine fields have been found to be negative for d- and f-shells and for np-shells with $n \geq 4$ (n is the principal quantum number), whereas for the 2p- and 3p-shells the fields are positive.

Now according to these results the hyperfine field A_d in (2) is negative. The measured magnetic susceptibility χ for pure Vanadium metal decreases with increasing temperature over the entire temperature range (300 ... 1900) K, Kriessman [11].

The measured χ in V_3Si is positive and decreases with increasing temperature up to 300 K (Clogston *et al.* [12]). Thus, if we suppose that χ in V_3Si decreases with the temperature over the range of (300 \cdots 1250) K, which is a reasonable assumption, then it is clear that the second term in (2) is negative and that its absolute value decreases with increasing temperature. From the fact that the first and the third term in (2) are positive it follows that the Knight shift $K(T)$ has to increase with increasing temperature. This is what our experimental results show as plotted in Figure 1. In the above model we presume that both the K_s and K_{orb} contributions in (2) are temperature-independent. As we have shown in an earlier work (Ploumbidis [13]) the orbital contribution to the Knight shift in certain transition metals may not only have the largest magnitude compared to the other contributions, but also the dominant temperature dependence. However, the model used here nevertheless allows a reasonable and consistent explanation of our experimental results concerning the V_3Si compound.

If there is any increase of K_{orb} with increasing temperature for V_3Si , it is still compatible with our interpretation given above for $K(T)$ in the frame of the model used. For a detailed quantitative analysis of the electronic structure of V_3Si in the high temperature range we need more results concerning different quantities such as relaxation times, magnetic susceptibility, density of states, and contact density.

As Fig. 2 shows, the ^{51}V Knight shift $K_{^{51}\text{V}}$ in VSi_2 is negative and has an absolute value which is one order of magnitude smaller than in V_3Si for temperatures at 1000 K.

The absolute value of $K_{^{51}\text{V}}$ in VSi_2 decreases with increasing temperature and becomes zero at 1250 K within the experimental error. Considering the shape of the $K_{^{51}\text{V}}(T)$ function for VSi_2 in Fig. 2 at high temperatures, one might expect that at 1500 K $K_{^{51}\text{V}}(T)$ should have positive values. Such an unusual temperature dependence of the Knight shift, changing from negative to positive values, has been observed by Setty and Mungurwadi [14] in the BiIn -system.

In further experiments we will study the behaviour of $K_{^{51}\text{V}}$ in VSi_2 at temperatures higher than 1400 K in order to get information about such an interesting possible change of the hyperfine field at the Vanadium nucleus.

It is expected that the diamagnetic contribution, particularly the diamagnetic core contribution, to the total susceptibility of VSi_2 is not negligibly small. We assume, however, that the temperature dependence of the diamagnetic susceptibility, and therefore the temperature dependence of the corresponding diamagnetic Knight shift term is negligibly small. There are several reasons which support this assumption.

Firstly, the diamagnetic susceptibility for different materials has been experimentally found to show an extremely weak temperature dependence as is the case for pure Si, which has been investigated by Glazov *et al.* [15]. Secondly, the temperature dependence of $K_{^{51}\text{V}}$ in VSi_2 , shown in Fig. 2, is not characteristic for diamagnetism because of its very large relative temperature variation. Our interpretation of the temperature behaviour of $K_{^{51}\text{V}}$ in VSi_2 is that there is a temperature dependent d-spin-p-spin mixing susceptibility and therefore a corresponding negative core polarization Knight shift contribution, whose absolute value decreases with increasing temperature. This is in agreement with our experimental results for $K_{^{51}\text{V}}$ in VSi_2 plotted in Fig. 2 against temperature.

In conclusion, the d-spin polarization in V_3Si is responsible for the temperature behaviour of $K_{^{51}\text{V}}$ in the normal state, for temperatures up to 1250 K. But according to the work of Clogston *et al.* [12], the same mechanism is also responsible for the $K_{^{51}\text{V}}$ value in the superconducting state, where 75% of the d-spin susceptibility disappears for very low temperatures below the transition temperature. On the other hand, in both the superconducting and the normal states the positive values of $K_{^{51}\text{V}}$ in V_3Si are governed by the nearly temperature independent orbital contribution to the Knight shift.

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