Knight Shift in the V\textsubscript{3}Ga Compound at High Temperatures

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The temperature dependence of the Knight shift of both \textsuperscript{51}V and \textsuperscript{71}Ga in the V\textsubscript{3}Ga compound has been measured over the entire range from 300 K to 1300 K. The results are discussed using a model based on the assumption that the core polarization contribution to the total Knight shift is the temperature dependent term.

Nuclear magnetic resonance studies have provided important information about the electronic properties of a wide variety of V\textsubscript{3}X compounds [1, 2]. It has been found that the compounds with the highest superconducting transition temperature \(T_c\) show the greatest temperature coefficient of the Vanadium Knight shift \(K_{\text{V}}\) in the non-superconducting state up to 400 K [1]. Therefore it is very interesting to ask how the various mechanisms contribute to the hyperfine properties and how the temperature variation influences the system.

In the present work we report on Knight shift measurements in the high temperature range (300-1300 K) concerning the isotopes \textsuperscript{51}V and \textsuperscript{71}Ga in V\textsubscript{3}Ga. Figure 1 shows the Knight shift \(K_{\text{V}}\) as a function of temperature. As a reference sample for the determination of \(K_{\text{V}}\) we used V\textsubscript{3}(SO\textsubscript{4})\textsubscript{3}. The average temperature coefficient \(\chi_1\) of \(K_{\text{V}}\) in V\textsubscript{3}Ga for the range (300-1300 K) is \(\chi_1 = 5.5 \cdot 10^{-5}\%K^{-1}\). This value of \(\chi_1\) is almost the same as the value of the temperature coefficient \(\chi_2\) of \(K_{\text{V}}\) in pure vanadium metal, \(\chi_2 = 4.5 \cdot 10^{-5}\%K^{-1}\), a value which was found for the same range (300-1300 K) in our earlier work [3]. Additionally, we found that \(K_{\text{V}}\) in V\textsubscript{3}Ga and in pure vanadium metal has almost the same value between 300 K and 1300 K. This is an indication that similar mechanisms are responsible for the hyperfine field at the \textsuperscript{51}V position in both systems. V\textsubscript{3}Ga and pure vanadium at high temperatures. As is reported in [1], the temperature coefficient of \(K_{\text{V}}\) in V\textsubscript{3}Ga amounts to \(39 \cdot 10^{-5}\%K^{-1}\) in the range between \(T_c\) and 300 K, whereas the temperature coefficient of \(K_{\text{V}}\) for pure vanadium amounts only to \(1 \cdot 10^{-5}\%K^{-1}\) between \(T_c\) and 300 K. The experimental results for the Knight shift \(K_{\text{Ga}}\) of \textsuperscript{71}Ga in the V\textsubscript{3}Ga compound for temperatures between 300 K and 1300 K are shown in Figure 2. For the determination of \(K_{\text{Ga}}\) we used GaCl\textsubscript{3} as a reference sample. \(K_{\text{Ga}}\) is negative over the entire temperature range and has between 300 K and 1300 K a temperature coefficient \(\beta = 23 \cdot 10^{-5}\%K^{-1}\), whereas \(\beta\) shows between \(T_c\) and 300 K the large value of \(170 \cdot 10^{-5}\%K^{-1}\).

A comparison between the results of our previous measurements on VSi [3] and those of the present work shows that the minority constituents X of the V\textsubscript{3}X compounds do not influence strongly the Vanadium Knight shift in the high temperature range. Over the entire range from 300 K up to 1300 K the magnitude of \(K_{\text{V}}\) in V\textsubscript{3}Ga is about 6% higher than the corresponding one in VSi.

A qualitative interpretation of the temperature dependence of \(K_{\text{V}}\) and \(K_{\text{Ga}}\) in V\textsubscript{3}Ga may be given in the frame of a model which has been used earlier to explain the results of Knight shift measurements of transition metal systems [4, 5]. In this model, the temperature dependence of the Knight shift \(K\) is assumed to be associated only with the d-spin contribution \(K_d\). The measured Knight shift \(K\) is separated as follows:

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

where \(K_s\) and \(K_{\text{orb}}\) 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 [6-8]. Additionally it is assumed that \(K_s\) and \(K_{\text{orb}}\) are positive, whereas \(K_d\) is negative [3, 6]. The negative sign of \(K_d\) results from estimates of the hyperfine fields associated with the core polarization due to half-filled d-shells. The estimates are based on experimental data and on exchange polarization calculations in the frame of the Hartree-Fock theory [9].

Now for the vanadium Knight shift \(K_{\text{V}}\) in V\textsubscript{3}Ga the positive contributions \(K_s\) and \(K_{\text{orb}}\) are dominant. With increasing temperature the absolute value of the negative \(K_d\) contribution decreases, and consequently the total value of \(K_{\text{V}}\) in (1) increases. This explains our experimental results plotted in Figure 1. As experimentally found, the Gallium Knight shift \(K_{\text{Ga}}\) is negative over the entire temperature range and shows a decreasing absolute value with increasing temperature (Figure 2). This behavior can be inter-
interpreted using the above model with the additional assumption that the dominant hyperfine field at the position of the Ga nucleus is due to the $K_4$ contribution. The mechanisms which cause the negative hyperfine field at the Ga nucleus are related with a strong mixture of the Ga 4p band with the V 3d band at the Fermi energy.

For a quantitative analysis of the electronic structure of the V$_3$X compounds in the high temperature range we need further experimental results. The experimental procedure of sample preparation and the high temperature spectrometer used for the measurements have been described elsewhere [3, 10].

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