Electrical Conductivity and NMR-Investigations in the A 15- and σ-Phase of V-Co Compounds in the High Temperature Range

D. Ploumbidis and G. Hüber

Institut für Atom- und Festkörperphysik der Freien Universität Berlin, Berlin (West)

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The electrical resistivity of the A15- and σ-phase of V-Co compounds has been measured in the temperature range 300 to 1300 K. Its temperature coefficient is found to be positive for the A15-phase, but negative for the σ-phase. For the same compounds we carried out ^{55}V- and ^{59}Co-Knight shift measurements in the high temperature range (300–1100 K). The ^{51}V-NMR-line corresponding to the central transition ($m = +\frac{1}{2} \rightarrow m = -\frac{1}{2}$) shows over the entire temperature range the characteristic splitting due to the second-order quadrupole interaction, whereas the ^{59}Co-NMR-line does not show any splitting. Using these NMR measurements we determined for the A15-phase the isotropic and anisotropic parts of the ^{51}V-Knight shift, the quadrupole coupling constant e^2qQ/h and the "line width" ΔB. The experimental results are discussed in the frame of models concerning hyperfine field and electric conductivity of transition metals and their alloys.

1. Introduction

Many contributions have been made towards a better understanding of the electronic and magnetic properties of transition metal alloys. But clearly we need more experimental and theoretical work to satisfactorily solve the problems concerning this complex field of metal physics. It is well known that in several transition metal alloys with room temperature resistivity $\varrho \leqq 100$ μΩ cm the temperature coefficient β of the resistivity is positive, whereas for alloys with $\varrho \geqq 200$ μΩ cm it is negative [1]. This behaviour of ϱ known as Mooij's rule has been discussed by many authors in the frame of different theoretical models, e.g. the Hubbard model [2], and the Mott-Anderson transition [3]. It is recognized that at high densities of states in the d band the scattering processes of the s electrons into the d band influence considerably the magnitude of the electrical resistivity. For compounds with low β values the strong scattering has been supposed to be of magnetic origin [4].

Experimental results show that in certain transition metals and alloys the paramagnetic susceptibility χ increases with increasing temperature T, whereas in others it decreases with increasing T. For the former group of materials the electrical resistivity ϱ at high temperatures increases more strongly than linearly with T, whereas for the latter ϱ increases less weakly than linearly with T. Therefore it is of considerable interest to carry out high temperature investigations concerning the electronic and magnetic structure of these materials. As is well known there is a very close relation between paramagnetic susceptibility and Knight shift. In this paper we report on the first high temperature ^{51}V- and ^{59}Co-Knight shift (K) and electrical resistivity measurements for the V_3Co (A15-phase) compound. For the σ-phase of V-Co we also carried out the first high temperature ^{51}V-Knight shift measurements, extending the measuring range of the electrical resistivity from 800 K to 1350 K. We discuss our experimental results in the frame of different models, giving satisfactory explanations for the behaviour of K and ϱ.

2. Experimental

All samples used for both the NMR and resistivity measurements were prepared starting from the same alloy material. The pure metals Co and V, with a purity of 99.995%, used for the alloys preparation, were supplied by Alfa Div. of Ventron Corporation. An arc-furnace with an argon (99.9995% purity) atmosphere was used for the melting procedure and alloy production.

For the NMR samples the starting material was crushed and sieved to prepare particles with a diam-

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Reprint requests to Ass. Prof. Dr. D. Ploumbidis, Freie Universität Berlin, Königin-Luise-Str. 28/30, D-1000 Berlin 33, Germany.

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eter less than 50 µm. The electrical resistivity samples were spark-erosion cut from the alloy bulk material. Before the measurement, each sample was chemically etched and annealed at 1400 K in vacuum (10^{-7} Torr) for 8 days. The resistivity experiments have been carried out at a frequency of 17 Hz. The concentration and purity controls of all alloys have been carried out with an x-ray fluorescence spectrometer. The major impurities of Fe, Cu and W have been found to be smaller than 200 ppm. Details of the experimental technique and NMR sample preparation are presented elsewhere [5].

3. Results

3.1. A-15 Phase

The NMR-signals of ^{51}V in V$_3$Co for the central transition ($m = +\frac{1}{2} \to m = -\frac{1}{2}$) at different temperature are shown in figure 1. A calculated NMR line shape (dotted curve) has been fitted to the experimental one (solid curve). For the fitting procedure we started from the relation (1) below, given in [6], [7] and [8], concerning the angle dependent resonance frequency ν for a constant external magnetic field, for an axial symmetry of the electric field gradient, for a nuclear spin $I = 7/2$ and for an isotropic Knight shift K_{iso} considerably smaller than unity ($K_{\text{iso}} \ll 1$):

$$\nu_{\frac{1}{2}\to-\frac{1}{2}} = \nu_0 + K_{\text{ax}}\,\nu_{\text{ref}}(3\mu^2 - 1) + \frac{15}{16}\frac{\nu_Q^2}{\nu_0}(1-\mu^2)(1-9\mu^2)\,, \tag{1}$$

where ν_0 is the frequency describing the center of the resonance line in the case of isotropic Knight shift without any quadrupolar perturbation, K_{ax} is the anisotropic part of the Knight shift, ν_{ref} is the resonance frequency of the nucleus in the reference compound, $\nu_Q = 3e^2 qQ/2I(2I-1)\,h$ is the expression for the pure quadrupole frequency, and $\mu = \cos\theta$, where θ is the angle between the crystal symmetry axis and the applied magnetic field. In our experiment we retained the resonance frequency constant and varied the magnetic field. The corresponding relation referring to the magnetic field is easily obtained from (1) using the elementary NMR relation between frequency and field:

$$B_{\frac{1}{2}\to-\frac{1}{2}} = B_0 - K_{\text{ax}} \cdot B_0(3\mu^2 - 1) - \frac{15\,B_Q^2}{16\,B_0}(1-\mu^2)(1-9\mu^2)\,. \tag{2}$$

For the fitting procedure we need a function f of the magnetic field B which describes our experimental NMR lineshape of the central resonance line in a powder sample as shown in Fig. 1 (solid curve). Equation (1) and therefore (2) are valid if the magnetic susceptibility tensor and the electric field gradient tensor have common principal axes. We assume that this is possible for the A15-structure because of its crystal symmetry. In connection to (2) we introduce the function f as follows:

$$f(B - B_0) = \int_{B_{Q,a}(-1)}^{B_{Q,a}(+1)} f_D(B - B_0 - B_{Q,a}) \cdot f_{Q,a}(B_{Q,a})\,\mathrm{d}B_{Q,a}\,, \tag{3}$$

where $B_0 = (2\pi/\gamma)\,\nu_0$ with γ the gyromagnetic ratio,

$$B_{Q,a} = -\,B_0 K_{\text{ax}}(3\mu^2 - 1) - (15\,B_Q^2/16\,B_0)(1-\mu^2)(1-9\mu^2)$$

and

$$B_Q = (2\pi/\gamma)\,\nu_Q\,.$$

The function f_D in (3) describes the NMR lineshape for crystallites with the same orientation and is approximated by the Gaussian function $f_D =$

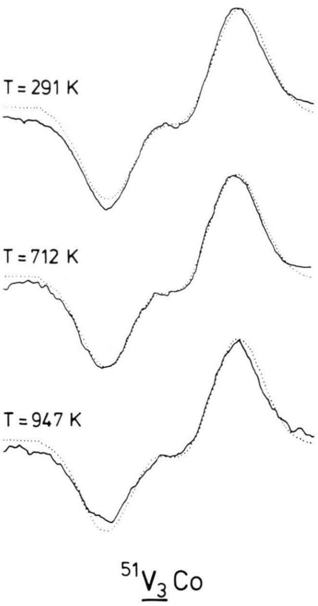

Fig. 1. Experimental (solid curve) and calculated (dotted curve) NMR lineshapes of the central transition ($m = \frac{1}{2} \to m = -\frac{1}{2}$) of the ^{51}V-resonance in V$_3$Co.

Temper. [K]	e^2qQ/h [MHz]	K_{iso} [%]	K_{ax} [%]	ΔB [mT]
291	4.140 ± 0.05	0.575 ± 0.003	0.045 ± 0.001	0.70 ± 0.01
451	4.140	0.575	0.045	0.70
546	4.140	0.575	0.045	0.70
668	4.138	0.575	0.045	0.69
712	4.135	0.572	0.044	0.69
790	4.143 ± 0.06	0.569	0.045 ± 0.003	0.68 ± 0.02
875	4.114 ± 0.07	0.571 ± 0.004	0.043	0.66
947	4.123	0.570	0.042	0.65
1.2	3.77	0.552	0.038	— [7]
20	1.0	0.53	—	— [9]
300	1.0	0.54	—	— [9]
4	4.1	—	—	— [10]

Table 1. The quadrupole coupling constant e^2qQ/h, the isotropic and anisotropic part of the Knight shift K_{iso} and K_{ax} respectively, and the "line width" ΔB and their temperature dependence, determined from the experimental and calculated NMR lineshape of the ^{51}V-resonance in V_3Co. For comparison we quote earlier works.

$\exp(-(B-B_0-B_{Q,a})^2/B^2)$. The function $f_{Q,a} \cdot (B_{Q,a})$ in (3), with the variable $B_{Q,a}$ given above, describes the angular dependent part of the lineshape function. Using (3) we calculated the NMR lineshape for the central transition ($m=\frac{1}{2}\rightarrow m=-\frac{1}{2}$) of the ^{51}V-resonance in V_3Co. This calculation has been carried out, firstly under the assumption that the NMR sample is made up of randomly oriented crystallites, and secondly under the consideration of the modulation and time constant influences connected with the lock-in-amplifier used for the NMR detection. The results of this calculation are shown in Fig. 1 and in Table 1, where at the end of the table four references concerning earlier results in the low temperature range are given for comparison. For the calculation of the lineshape and the fitting parameters given in Table 1 we used the computer "Apple 48 K".

The temperature dependence of the ^{59}Co-Knight shift in V_3Co is shown in Figure 2. In contrast to the ^{51}V Knight shift (see Table 1) the ^{59}Co-Knight shift shows a temperature dependence which clearly lies outside the experimental error. A comparison between Figs. 1 and 2 shows that the ^{59}Co resonance line does not show any splitting. This is because of the cubic symmetry of the Co-sublattice in the V_3Co-structure.

Figure 3 shows the temperature dependence of the electrical resistivity ϱ of the V_3Co compound. There is a less-than-linear rise in ϱ when the temperature T increases. This behaviour of ϱ at high temperatures for d-band compounds has been called "resistivity saturation" [11]. The room temperature

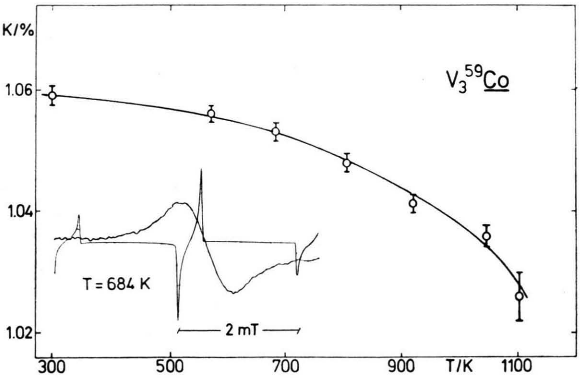

Fig. 2. The temperature dependence of the ^{59}Co-Knight shift in V_3Co. In contrast to the ^{51}V-resonance in this compound, the ^{59}Co-resonance does not show any splitting; this is due to the cubic sublattice of the Co-atoms in V_3Co. The three sharp signals together with the ^{59}Co-signal are proton resonances serving to control the external magnetic field.

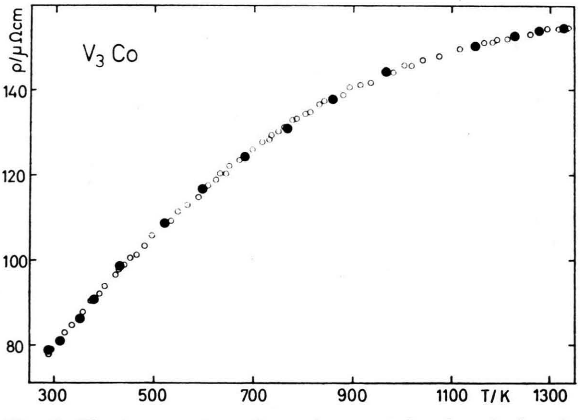

Fig. 3. The temperature dependence of the electrical resistivity of V_3Co. Open circles denote increasing temperature, closed circles decreasing temperature.

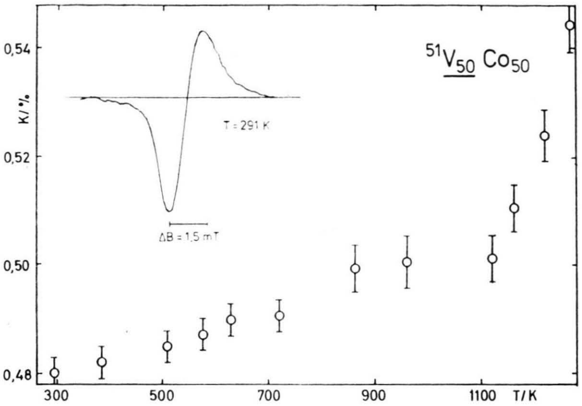

Fig. 4. The temperature dependence of the ^{51}V-Knight shift in the 50 at.% V-50 at.% Co-compound (σ-phase). The asymmetry of the resonance signal decreases with increasing temperature.

value $\varrho \approx 80$ μΩ cm ± 5% and a saturation value of nearly 150 μΩ cm at 1350 K lie in the characteristic range of resistivity for A15-structure metals.

3.2. *σ-Phase*

Figure 4 shows the temperature dependence of the ^{51}V-Knight shift in the 50 at.-% V-50 at.-% Co-compound (σ-phase). The ^{59}Co-resonance could not be observed in the high temperature range for this compound. Nakajima et al. [12] report on the ^{59}Co-resonance in a σ-phase Vanadium-Cobalt compound at 4.2 K. They find a very large linewidth of about 70 G. The lineshape of the ^{51}V-resonance in the σ-phase does not show any splitting as is indicated in Figure 4. The asymmetry of the lineshape becomes weaker with increasing temperature. The temperature dependence of the electrical resistivity ϱ of the 50 at.-%V-50 at.-% Co-compound is presented in Figure 5.

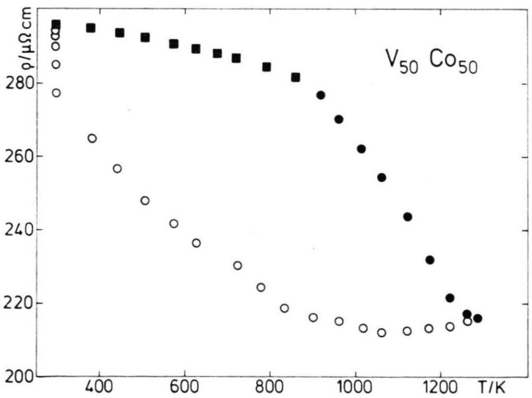

Fig. 5. The temperature dependence of the electrical resistivity ϱ of the 50 at.% V-50 at.% Co-compound. The variation of ϱ with temperature is reversible in the range 290 to 860 K (closed aquares).

In contrast to the temperature behaviour of ϱ in the A15-phase its temperature coefficient in the σ-phase is negative. Additionally, figure 5 shows some other striking features of ϱ. The variation of ϱ with temperature is reversible in the range 290 to 860 K (the measuring points for this range are labelled with closed squares). For higher temperatures $\varrho(T)$ shows a pronounced hysteresis. The cooling procedure from about 1200 K down to 290 K, i.e. until the resistivity has its initial value, takes a very long time (30 days). The measurements have been repeated several times in a time interval of three months and the ϱ values have been found to be reproducible within ±2%.

4. Discussion

As Table 1 shows both parts of the ^{51}V-Knight shift are temperature independent within the experimental error. This is of particular interest because vanadium intermetallic compounds V_3X (where X = Si, Co, Ga, Au, Pt, ...) show Knight shifts with a characteristic temperature behaviour, which have been correlated with their superconducting transition temperature T_c [9]. The V_3X-systems with the highest T_c have a Vanadium Knight shift with the strongest temperature variation, while systems with low T_c or without superconducting properties in the temperature range of investigation, have almost temperature independent Knight shift. The V_3Co system does not become a superconductor for temperatures down to 15 mK [13], so that it belongs to the latter class of V_3X compounds. Systems such as V_3Si and V_3Ga have been investigated in an extended temperature range and have been found to belong to the former class [9], [14], [15].

The weak decrease of $e^2 qQ/h$ with increasing temperature (see Table 1) is mainly due to the decrease of the electric field gradient with increasing temperature. The decrease of the linewidth "ΔB" with increasing temperature is partly due to the decrease of the field gradient and partly to the reduction of the dipolar interaction.

An interesting case is the ^{59}Co-Knight shift K_{Co} in V_3Co and its temperature dependence shown in Figure 2. In other A15-structure compounds, such as V_3Pt and V_3Ga, K_{Pt} and K_{Ga} are negative and their absolute values show a strong decrease with increasing temperature. In contrast, K_{Co} in V_3Co is positive and shows a temperature reduction more than 10 times smaller than that of K_{Pt} and K_{Ga} in V_3Pt and V_3Ga respectively. The Knight shift of Ga in pure Gallium metal is positive whereas it is negative in V_3Ga. Thus, it is possible that due to the formation of the *intermetallic system* V_3Ga the polarization of the outer s-like electrons is reversed or that a local core-polarization effect creates a dominant negative hyperfine magnetic field at the site of the Ga-nucleus. In alloys of metallic solutes in metallic solvents, where no intermetallic bonds dominate the system, all known Knight shifts have been found to be positive. So the V_3Co system rather seems to be a "metallic alloy" than an "intermetallic compound". This clasification is supported by our experimental results concerning the electrical resistivity ϱ of V_3Co shown in Figure 3. Both the room temperature value and the temperature variation of $\varrho(V_3Co)$ are characteristic for "metallic alloys".

As mentioned above, it is recognized that in A15-structure d-band compounds, with ϱ nearly 80 μΩ cm, a kind of resistivity saturation occurs at elevated temperatures. A maximum resistivity with a value $\varrho_{max} \approx 150$ μΩ cm, (which varies somewhat with material) sets in. The "shunt resistor model" describes phenomenologically the $\varrho(T)$ behaviour and says that

$$\varrho(T) = (\varrho_{ph}(T) \cdot \varrho_{max})/(\varrho_{ph}(T) + \varrho_{max}), \quad (4)$$

where $\varrho_{ph}(T)$ is the temperature dependent part of the resistivity mainly determined by the electron-phonon scattering processes. If $\varrho_{ph}(T)$ is large enough (in the range of 1000 μΩ cm and higher) and increases linearly with the temperature (which is a usual approximation up to 1000 K) then $\varrho(T)$ in (4) tends toward ϱ_{max} and describes satisfactorily the experimental results shown in Figure 3.

In order to obtain a better insight into the magnetic and electronic behaviour of the V-Co system in the A15- and σ-phase we also investigated the Knight shift and electrical resistivity in the σ-phase $V_{50}Co_{50}$ alloy. A possible interpretation for the temperature dependence of K_{51_V} shown in Figure 4 may be given in terms of a model, which has been in the past sucessfully applied in transition pure metals and alloys [16], [17]. We write for $K_{51_V}(T)$:

$$K_{51_V}(T) = A_s \chi_s + A_d \chi_d(T) + A_{orb} \chi_{orb}, \quad (5)$$

where χ_s, χ_d and χ_{orb} are the s-spin-, d-spin- and orbital-susceptibility respectively, and

$$A_s = \frac{\Omega}{\mu_B} B_{hf}(s), \quad A_d = \frac{\Omega}{\mu_B} B_{hf}(d)$$

and

$$A_{orb} = \frac{\Omega}{\mu_B} B_{hf}(orb)$$

are factors related to the corresponsing hyperfine fields; μ_B is the Bohr magneton and Ω is the atomic volume.

According to experimental data and exchange polarization calculations the core-polarization hyperfine field of d-shells is negative [8]. Thus, if we suppose that A_d in (5) has a negative value, a decrease of $\chi_d(T)$ with increasing temperature causes a decrease of the negative contribution to the Knight shift and so the entire Knight shift $K_{51_V}(T)$ in (5) increases with increasing temperature. This is what we found experimentally as shown in Figure 4.

Earlier electrical resistivity investigations show that several transition metal alloys have a ϱ with a negative temperature coefficient β [1]. As presented in Figure 5, the resistivity of the $V_{50}Co_{50}$-alloy (σ-phase) is characterized by a negative β in contrast to the positive β of the resistivity in the $V_{75}Co_{25}$-compound (Figure 3). As mentioned above, this behaviour can be classified phenomenologically with the help of Mooij's rule [1]. This rule has been frequently discussed by many authors starting from different models. All these treatments give more or less qualitative approximations describing the experimental results. Recently, Elk et al. [2] calculated the electrical resistivity of concentrated transition metal alloys in the frame of an extended Hubbard model. They found that due to influence of: a) disorder processes, b) electron-electron correlations and c) s-d hybridization the electrical resistivity varies strongly with the electron density. For regions where the resistivity is large, there is a negative β; whereas for regions with small resistivity, β is positive. This is in qualitative agreement with our experimental results plotted in Fig. 3 and Figure 5. It is evident from these studies that further experimental and theoretical information is needed for a deeper, mainly quantitative understanding of the complex behaviour of the magnetic and electronic properties of these materials.

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