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THE ELECTRONIC STRUCTURE OF Sc *AND THE MECHANISM OF THE KNIGHT SHIFT IN* $ScAl_2$ *AND* $ScAl_3$

V. I. CHECHERNIKOV, V. I. NEDEL'KO and A. V. VEDYAEV

Moscow State University

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On the basis of experimental data on the magnetic susceptibility of Sc and of the compounds $ScAl_2$ and $ScAl_3$, as well as on the Knight shift in these compounds, information is obtained on the distribution of the spin density in metallic Sc. It is shown that the anisotropy of the electron cloud, which is elongated along the hexagonal axis, is determined by its diamagnetic susceptibility. An important role is played in the production of the fields at the nuclei by the collectivized d-electrons of Sc, the influence of which depends on the structure of the compounds.

As is well known, Sc, having one electron in the d-shell, heads up the series of transition metals. Therefore, information concerning the structure of the electron cloud of Sc in the metallic state, and also of some of its intermetallic compounds, is of fundamental interest for the clarification of the role of the electrons in transition metals in general. We have attempted to obtain such information from the experimental data on the magnetic susceptibility of single-crystal Sc and the intermetallic compounds $ScAl_2$ and $ScAl_3$, and also from data on the magnitude of the fields at the Al nuclei in these compounds.

1. MAGNETIC SUSCEPTIBILITY

The susceptibility of single-crystal Sc was measured along the directions parallel and perpendicular to the hexagonal axis, and obtained at room temperature the following results: $\chi_{\parallel} = 294 \times 10^{-6}$ and $\chi_{\perp} = 232 \times 10^{-6}$. In the case of the polycrystalline compounds $ScAl_2$ and $ScAl_3$, the magnetic susceptibility is respectively 125×10^{-5} and 115×10^{-6}. The total magnetic susceptibility of Sc and of its compounds can be written in the form

$$\chi = \chi_{\text{dia}} + \chi_{\text{orb}} + \chi_{sd}, \tag{1}$$

where χ_{dia}—diamagnetic susceptibility, χ_{orb}—orbital contribution to the susceptibility of the d-electrons, and χ_{sd}—Pauli susceptibility of the collectivized system of conduction electrons and d-electrons.

To explain the difference between $\chi_{\parallel}$ and $\chi_{\perp}$ in single-crystal Sc, the authors have proposed earlier[1] a model of an electron cloud elongated along the hexagonal axis, the anisotropy of the magnetic susceptibility of which explained quite satisfactorily the experimentally observed anisotropy. Starting from this model, it was possible to obtain an estimate for the total value of the diamagnetic contribution to the susceptibility of Sc, which turned out to be -38×10^{-6}. Thus, we are left with 300×10^{-6} for the remaining contributions of the orbital angular momentum and the Pauli susceptibility, and according to the estimate of the Gardner and Penfold[2], the main contribution is made by the Pauli susceptibility of the d-electrons.

Similar estimates made by us for the compounds $ScAl_2$ and $ScAl_3$ allow us to state that χ_{sd} in both compounds are approximately the same and of the order of 80×10^{-6}. In addition to the susceptibility χ_{d}, the third term of formula (1) includes also the Pauli susceptibility χ_{s} of the conduction s-electrons. An estimate of the value of χ_{s} in aluminum and in the compounds $ScAl_2$ and $ScAl_3$ shows that $\chi_{\text{s}} \sim 12 \times 10^{-6}$ in Al and in $ScAl_3$, and $\chi_{\text{s}} \sim 9 \times 10^{-6}$ in $ScAl_2$. These results will be used subsequently to discuss the mechanism whereby the hyperfine field is produced at the nucleus in these compounds.

2. KNIGHT SHIFT

We measured the Knight shift in $ScAl_2$ and $ScAl_3$ at room temperature in magnetic fields 10–15 kOe with the aid of a NMR spectrometer intended for observation of broad lines.

The measurement error was due essentially to the instability of the apparatus in the class of instruments with which the frequency was measured. The total error was ±0.01%.

The results of the investigation have shown that the night shift in pure Al and in $ScAl_3$ is positive and equals 0.16%, while in $ScAl_2$ it decreases rapidly and has a weak dependence on the magnetic field intensity. Thus the shift is −0.02% at H = 11 kOe, and +0.02% at H = 15 kOe.

The Knight shift in transition metals, according to Clogston[3], can be written in the form

$$K = \alpha_1\chi_s + \alpha_2\chi_s - \beta\chi_d, \tag{2}$$

where $\alpha_1\chi_{\text{s}}$ is the direct contribution of the conduction electrons. Here χ_{s}—Pauli susceptibility; $\alpha_1 = (8/3)\pi\langle|\psi(0)|^2\rangle_{\text{F}}$, where $\langle|\psi(0)|^2\rangle_{\text{F}}$ is calculated on the Fermi surface and represents the average probability density of finding the electron at the location of the nucleus; $\alpha_2\chi_{\text{s}}$—contribution due to the polarization of the internal electrons by the conduction electrons; $\beta\chi_{\text{d}}$—contribution to the Knight shift as a result of the polarization of the internal s-electrons by the d-electron[4]. The coefficient χ is given by

$$\beta = \frac{8\pi}{3}\frac{2}{A_F}\left\langle \int_0^{r_s} \psi_{k_F}(1)\,\delta\psi_{s,N}(1)\,\psi^*_{k_F}(2)\,\psi_{s,N}(2)\,\frac{d\tau_1 d\tau_2}{r_{12}} \right\rangle_F, \tag{3}$$

where A_{F}—area of Fermi surface, ψ_{k_F}—wave function of the d-electrons, ψ_{sN}—wave function of the internal f-electrons, and $\delta\psi_{s,N}$—perturbed function of the internal s-electrons. Inasmuch as a theoretical calculations and experiment[5] have shown that the second term of (2) is very small for aluminum, and is of the same order of magnitude in the compounds investigated by us, the expression for the Knight shift of the given Al compounds can be written in the form

$$K = \alpha_1\chi_s - \beta\chi_d. \tag{4}$$

The negative term $\beta\chi_d$ can be assumed comparable with the direct contribution, or even larger. Thus, in Sc for a direct shift of 0.4%, the shift due to this term is −0.28%[6], and in the compound AlV this contribution is even larger than the direct contribution, thus explaining the negative Knight shift in this compound.

In the compounds $ScAl_2$ and $ScAl_3$ investigated by us, as already noted above, the Knight shift is different, and in the case of $ScAl_3$ the shift is the same as for pure aluminum, whereas in $ScAl_2$ the shift is much smaller. The decrease of the Knight shift in the latter compound is attributed by us to the large magnitude of the negative term $-\beta\chi_d$ in formula (4). It should be noted here that, as shown by our measurements, the susceptibilities and the presented estimate of the individual contributions χ_d in the compounds $ScAl_2$ and $ScAl_3$ are the same, but the values of β, as will be shown below, greatly differ (β in the case of $ScAl_2$ is much larger than β in the case of $ScAl_3$), thus explaining the obtained results.

The coefficient β was estimated in accordance with formula (3) and for the wave functions of the d-electrons ψ_{k_F} we used the expressions obtained in the tight-binding approximation.

It should be noted that in $ScAl_2$ and $ScAl_3$ the distances between the Sc and Al atoms are approximately the same at ≈ 3 Å[7], but the crystal structures are different. The symmetry of the wave d-functions is such that whereas in $ScAl_3$, which is the structure of $AuCu_3$, an important role is played in the calculation of the integrals in (3) by functions of the type d_{xy}, d_{zx} and d_{yx}, in the compound $ScAl_2$, which has the structure of $MgCu_2$, it is also necessary to take into account the functions d_{z^2} and $d_{x^2-y^2}$.

Our estimate of the contributions of these two functions to the coefficient shows that the contributions from the functions d_{xy}, d_{yz}, and d_{zx} amount to several per cent of the contributions of the functions d_{z^2} and $d_{x^2-y^2}$, thus explaining why the coefficient β, meaning also the polarization term of the d-electrons, is much larger in $ScAl_2$ than in $ScAl_3$. Thus, the Knight shift in compounds of Sc with Al depends on their crystal structure via the mechanism of polarization of the internal s-electrons by the external d-electrons. A similar behavior of the Knight shift was observed also in $LaAl_2$[8], which has the same structure as $ScAl_2$.

As already noted, the Knight shift in $ScAl_2$ increases with increasing magnetic field. Inasmuch as the coefficients α and β do not depend on H, this change should be determined by the susceptibilities χ_s and χ_d.

The dependences of these susceptibilities on the field are given by

$$\chi_s(H) = \chi_s(1 - B_sH^2), \tag{5}$$
$$\chi_d(H) = \chi_d(1 - B_dH^2),$$

where $B_d \gg B_s$. It follows therefore that the susceptibility χ_d decreases with increasing H more rapidly than χ_s, and according to (4) the Knight shift in the compound $ScAl_2$ should increase with increasing field. We note that if we determine the Knight shift by extrapolation to $H \to \infty$ and calculate $\alpha_1\chi_s$, using the values of χ_s from susceptibility data, then we obtain the same value, namely ≈ 0.12%.

Thus, the dependence of the Knight shift on the magnetic field in $ScAl_2$ is due to the field dependence of the Pauli part of the susceptibility of the d-electrons of Sc.

On the whole, the model employed by us to explain the Knight shift in the investigated compounds $ScAl_2$ and $ScAl_3$ makes it possible to conclude that the cloud of collectivized d-electrons conserves to a considerable degree the symmetry of the wave functions of the d-electrons of the isolated atoms.

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