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Relativistic spin polarized *ab initio* calculations of the anisotropy and temperature dependence of the paramagnetic spin susceptibility of scandium and yttrium

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Abstract. Recently, a new formalism for the temperature dependence of the anisotropy of the paramagnetic spin susceptibility of metals has been developed. We apply this theory to paramagnetic metals HCP scandium and yttrium. Calculated results show the paramagnetic spin susceptibility along the c axis, χ_c, to be greater than that along the a axis, χ_a, within the temperature range of 0–300 K for both metals. These results are consistent with experiment, when the Van Vleck orbital susceptibility is taken into account. Our results also suggest that the magnetic moments of transition metal impurities in Sc and Y will align with the c axis.

1. Introduction

A new formalism for the paramagnetic spin susceptibility (PSS) was given in our previous paper [1]. This formula indicates the preferred direction of magnetization, i.e. an easy axis, and is able to describe a temperature dependence of the anisotropy of the PSS. Based upon a relativistic spin polarized multiple scattering theory, it is a 'first principles' framework, namely, it is parameter free. It is significant for the study of magnetic anisotropic effects that both fully relativistic and spin polarized effects are treated on an equal footing.

In our previous paper [1], we applied this theory to both structural phases (HCP and FCC) of paramagnetic cobalt and found the temperature dependence of the easy axis of the magnetization. Our results show that the easy axis changes from the a-axis to the c-axis with decreasing temperature in HCP Co. In this paper, we calculate the PSS of HCP Scandium (Sc) and yttrium (Y) applying our theory to paramagnetic metals. The orientation of dilute magnetic impurities and its temperature dependence in these metals is an especially interesting problem. Our results suggest a preferred orientation of magnetic impurities in Sc and Y.

Sc and Y belong to the same IIIA group of the periodic table and are often classified with lanthanides (rare-earth metals). Experimental studies of the magnetic susceptibility of Sc have been made by several authors (see [2]). However these experimental results are not always in good agreement with each other because of the difficulty in making

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high-purity crystals of Sc. Spedding and Croat [2] measured the magnetic susceptibility of highly pure Sc single crystals. They found χ_a, the susceptibility along the a-axis, to be greater than χ_c, that along the c-axis, within the temperature range of 1.5–300 K. A maximum was observed at 30 K in the temperature dependence of the susceptibility. Stierman *et al* [3] measured the magnetic susceptibility of a Sc crystal of higher purity. Their results are in good agreement with those of Spedding and Croat above 50 K, but there is a small difference between the experiments at low temperatures.

On the theory side, many band-structure calculations have been carried out [4–8]. They differ from each other on several points, and they do not agree well with the only experimental results on the de Haas–Van Alphen effect [9] which we have found. Nevertheless, Das [6] calculated a temperature dependence of the magnetic susceptibility from his band structure and obtained excellent agreement with the experiment. MacDonald *et al* [10] calculated a Stoner enhancement factor from local spin density functional theory and they also obtained good agreement with experimental results. The maximum of the susceptibility was explained with a Fermi-liquid theory by Barnea [11].

Experimental studies of the magnetic susceptibility of yttrium have also been performed [12–14]. Like Sc, χ_a was found to be greater than χ_c. A maximum of the temperature dependence of susceptibility was observed at 300 K. Band-structure calculations have been made [4, 15], but there have been few compared with the number for Sc. On the other hand, experiments on the de Haas–van Alphen effect have been performed by several authors [16–18]. The results of de Haas–van Alphen effects have been explained well by the Fermi-surface model of Loucks [15]. There has been little theoretical investigation of the magnetic susceptibility and its temperature dependence. Misawa and Kanematsu [19] explained the maximum in the temperature dependence using Fermi-liquid theory.

In this paper, we calculate the anisotropy and temperature dependence of the PSS for Sc and Y by our first-principles theory. To compare our results directly with experiment it is necessary to calculate the van Vleck orbital susceptibility and the diamagnetic susceptibility. Spin fluctuation effects are also important for these metals. Although these aspects are not included here, we use estimates of the first two given by previous works [6, 10]. We find that the temperature dependence of the anisotropy found in experiment follows that of our calculated PSS. We also draw conclusions from our calculations about the preferred orientations of transition metal impurities in Sc and Y.

2. Theory

A brief outline of the new formalism of the PSS is given in this section. A more complete description is provided in [1]. The starting point is consideration of the leading response of the system to a small applied magnetic field. The effective magnetic field $B^{eff}(n, m)$ is given by [20],

$$B^{eff}(n, m) = \mu_B(B^{ext}(r) - B^{xc}[n, m]m) \tag{1}$$

where B^{ext} is a fictional magnetic field coupling to the spin of the electron only (neglecting the orbital part), and B^{xc} is the exchange–correlation term determined approximately by local spin density functional theory.

A Green function for an effective one-electron Kohn–Sham–Dirac equation satisfies the following equation.

$$[-i\hbar c\alpha \cdot p + \beta mc^2 + 1V^{\text{eff}}[n, m] - \beta\sigma \cdot B^{\text{eff}}[n, m] - \varepsilon]G(r, r'; \varepsilon) = 1\delta(r - r') \qquad (2)$$

where V^{eff} is an effective one-electron potential, α and β are standard Dirac matrices and σ are the 4×4 Pauli matrices. All other symbols have their usual definitions. A magnetic moment $m(r)$ (spin only) which is induced by the external field B^{ext} is given by

$$m(r_i) = -\frac{1}{\pi}\text{tr}\,\beta\sigma\,\text{Im}\int f(\varepsilon - \nu)G(r_i, r_i; \varepsilon)\,\text{d}\varepsilon \qquad (3)$$

where $f(\varepsilon - \nu)$ is a Fermi–Dirac function and ν is the chemical potential. The Green function which is a solution of equation (2) is approximated by

$$G(r_i, r_i; \varepsilon) = G_0(r_i, r_i; \varepsilon) - \sum_j \int G_0(r_i, r'_j; \varepsilon)\beta\sigma \cdot B^{\text{eff}}(r'_j)G_0(r'_j, r_i; \varepsilon)\,\text{d}r'_j. \qquad (4)$$

$G_0(r, r'; \varepsilon)$ is the Green function corresponding to the system with zero external magnetic field B^{eff}. This quantity can be written using relativistic multiple scattering theory [21, 22] (equations (5) and (6) of [1]).

In order to take into account the spatial dependence of the magnetic field explicitly, we introduce the following rotation operator in spin space.

$$\mathscr{R}(\theta, \varphi) = \begin{pmatrix} \cos(\theta/2)\,e^{-i\varphi/2} & -\sin(\theta/2)\,e^{-i\varphi/2} \\ \sin(\theta/2)\,e^{i\varphi/2} & \cos(\theta/2)\,e^{i\varphi/2} \end{pmatrix} \qquad (5)$$

where the angles θ and φ describe the orientation of B^{eff} with respect to the crystal axes. We can express the $\sigma \cdot B^{\text{eff}}$ in eq. (4) as follows,

$$\sigma \cdot B^{\text{eff}} = \mathscr{R}(\theta, \varphi)\sigma_z\,|B^{\text{eff}}|\mathscr{R}^\dagger(\theta, \varphi). \qquad (6)$$

The muffin-tin approximation is used. From equation (3), we can write an expression, involving the PSS, of the following form.

$$m = \int^{r_{mt}} m(r_i)\,\text{d}r_i = \chi_0(\theta, \varphi)B^{\text{ext}} + I\chi_0(\theta, \varphi)m. \qquad (7)$$

Finally a temperature Green function is introduced to take into account the temperature dependence. Consequently we obtain a formula for the PSS.

$$\chi^{\text{PSS}} = m/B = \chi_0(\theta, \varphi, T)/[1 - I\chi_0(\theta, \varphi, T)]. \qquad (8)$$

Equation (8) has the form of a Stoner-type formula. Relativistic effects (spin–orbit coupling) have caused the θ, φ dependence. The quantity I can be called a generalized Stoner parameter.

3. Results and discussion

Relativistic band structures of Sc and Y calculated by the relativistic KKR method are shown in figure 1. The lattice constants used are shown in table 1. Input muffin-tin potentials are produced by SCF non-relativistic APW calculations. The densities of states (DOS) are shown in figure 2. The Fermi energy is indicated by an arrow, i.e., $\varepsilon_F = 0.479$ Ryd for Sc and 0.435 Ryd for Y. The DOS at the Fermi energy are listed in table 2
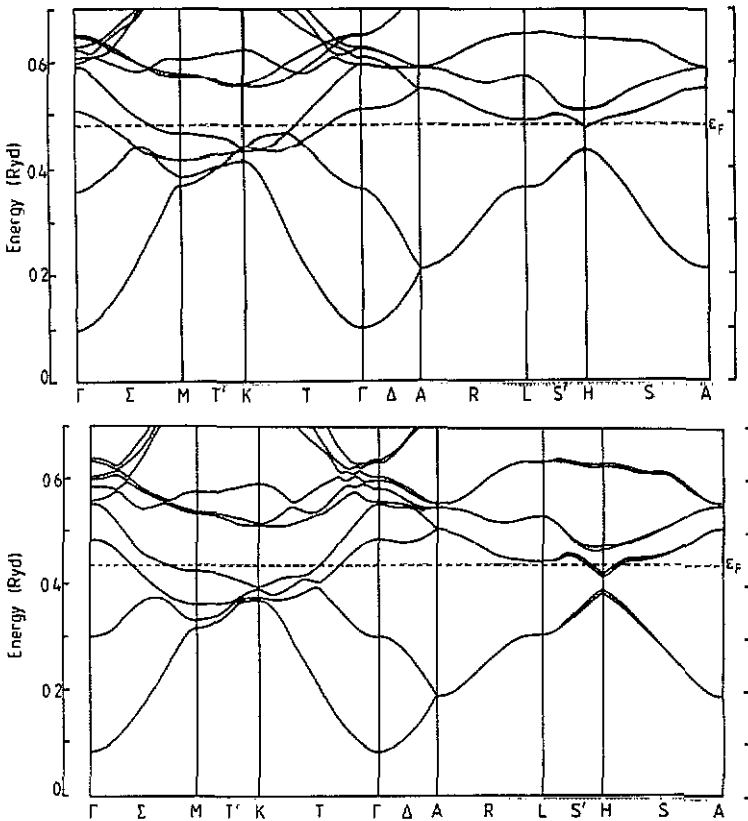
Figure 1. (a) Relativistic band structure of HCP Sc and (b) that of HCP Y.

Table 1. Lattice constants of Sc and Y (in atomic units).

	a	c	c/a	Ratio of ideal value†
Sc	6.23988	9.91351	1.58873	-2.7103%
Y	6.89259	10.82927	1.57115	-3.7873%

† $(c/a - \sqrt{8/3})/\sqrt{8/3}$.

together with those from other calculations for comparison. Apart from some small differences they are consistent with each other. It seems that these values strongly depend on the lattice parameters and the method for the treatment of the exchange correlation potential.

The PSS were evaluated via equation (8) using these Fermi energies and SCF muffin-tin potentials. The generalized Stoner parameters $I(T)$ are almost independent of temperature, with values of about 0.0271 Ryd for Sc and 0.0275 Ryd for Y. We calculated an enhancement value at 0 K, i.e., $1/(1 - I\chi_0^{DOS})$, where χ_0^{DOS} is estimated from the DOS at the Fermi energies. These are listed in table 3. For Sc, the present value is good agreement with the other investigations. (The result of Das was obtained by parameter fitting with experimental data.) The enhanced PSS at 0 K, $\chi^{enh}(0) = \chi_0^{DOS}/(1 - I\chi_0^{DOS})$,
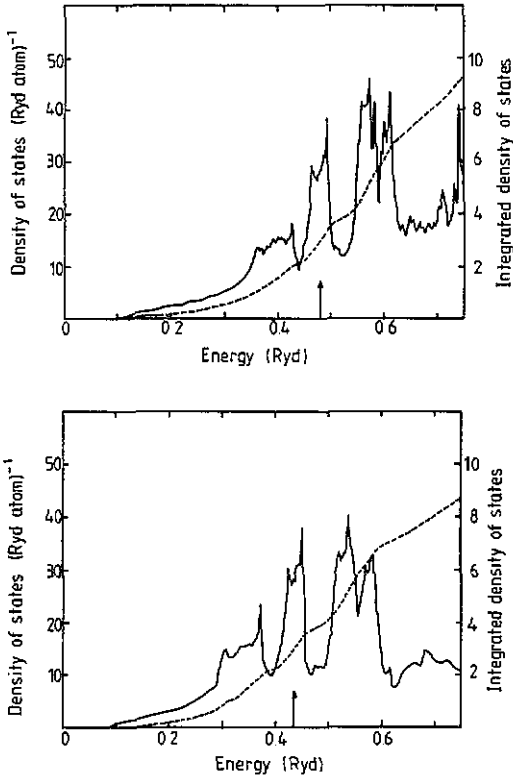
Figure 2. (*a*) Density of states (full curve) and integrated density of states (broken curve) of HCP Sc and (*b*) that of HCP Y.

Table 2. Density of states at the Fermi energy in (atom Ryd)$^{-1}$.

Sc		Y	
Present work	27.6	Present work	27.9
Das	26.8	Loucks	26.8
MacDonald *et al*	29.4	NRAPW	31.8
Fleming and Loucks	31.0		
NRAPW†	30.5		

† NRAPW: our non-relativistic APW calculation.

Table 3. The generalized Stoner parameter (atomic units) and the enhanced PSS (10^{-6} emu g^{-1}).

		I (au)	$1/(1 - I\chi^{DOS})$	$\chi^{enh}(0)$	χ^{VV}	χ^{dia}	χ^{total}
Sc	Present	0.0271	4.08	6.00	2.84	−0.60	8.24
	Das	0.0293	4.60	6.52	2.84	−0.93	8.43
	MacDonald *et al*	0.0256	4.03	6.25	2.71	−0.60	8.36
	Experiment	—	—	—	—	—	8.45
	FCC†	0.0253					
Y	Present	0.0275	4.32	6.22			
	Experiment [13]	—	—	—	—	—	2.22
	FCC†	0.0244					

† Values for FCC were calculated by Morruzi *et al* [23].
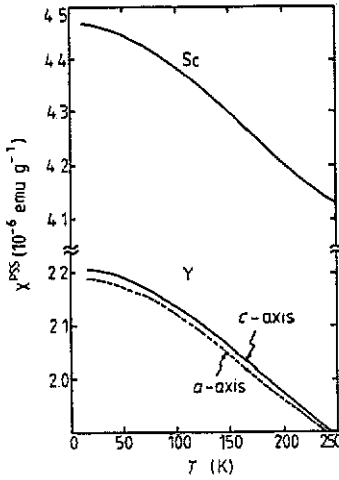
Figure 3. Temperature dependence of the paramagnetic spin susceptibilities.

agrees with the experimental value very well, if we take into account the orbital (van Vleck) and diamagnetic susceptibilities from previous works [6, 10]. On the other hand, in the case of Y, there is no calculation with which we can compare our result. The enhanced PSS seems too large in comparison with the experimental value. The band structure calculations of Y explain experimental data well, for example, de Haas–van Alphen effects, specific heat etc. We therefore think that the DOS at the Fermi energy is accurate. It may be that the generalized Stoner parameter is slightly overestimated and that the spin fluctuation effect may also be important. Indeed, the calculated value of the Stoner parameter by Moruzzi *et al* [23] is 0.0244, but their result is that for FCC Y. We found that a difference between the values for FCC and HCP is very small in the case of cobalt. If the value of I for HCP Y is 0.025 (the calculated value is 0.0275), the enhancement factor decreases substantially i.e. $4.3 \rightarrow 3.3$. Consequently, the enhanced PSS become about 25% less than the present value, demonstrating its sensitivity to the generalized Stoner parameter. Of course, it might be that the diamagnetic susceptibility of Y is larger than that of Sc too.

In figure 3, the calculated temperature dependences of the PSS are shown. We found χ_c^{PSS} to be greater than χ_a^{PSS} for both metals in this temperature range. Because $\chi_c^{PSS} - \chi_a^{PSS}$ has a very small value for Sc, it is not shown in this figure. We obtain $\chi_c^{PSS} - \chi_a^{PSS}$ to be about 0.0018×10^{-6} emu g^{-1} at 25 K. This quantity decreases with temperature. On the other hand, $\chi_c^{PSS} - \chi_a^{PSS}$ for Y at 25 K is 0.0174×10^{-6} emu g^{-1}, and also decreases with temperature. The temperature dependence of the $\chi_c^{PSS} - \chi_a^{PSS}$ is shown in figure 4. The anisotropy of Y is about ten times greater than that of Sc. This is due to the relativistic effects being more important for the heavier Y. The experimental results of Spedding and Croat found $\chi_a > \chi_c$. This discrepancy could be attributed to the contribution from anisotropy of orbital susceptibility. Das calculated this quantity for Sc. He found that $\chi_a^{VV} > \chi_c^{VV}$ and that these values are insensitive to changes in temperature. His estimated value of $\chi_a^{VV} - \chi_c^{VV}$ is slightly greater than the experimental anisotropy of the total susceptibility, $\chi_a - \chi_c$. If we can regard the difference between the anisotropy of the total susceptibility and that of the orbital one to be due to the anisotropy of PSS, then
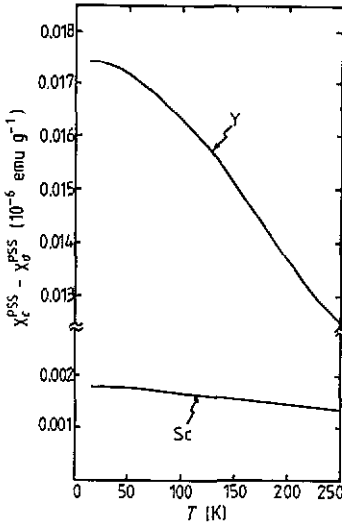
Figure 4. Temperature dependence of the anisotropies $\chi_c^{PSS} - \chi_a^{PSS}$ for Sc and Y.

$\chi_c^{PSS} > \chi_a^{PSS}$. This is consistent with our result. However, it is necessary to make accurate calculations of the orbital susceptibility to draw this conclusion firmly.

Unfortunately, there is no estimate of the anisotropy of the orbital susceptibility of Y, so we are unable to make a similar rough comparison. However, it seems likely that a similar situation occurs.

The temperature dependences of the PSS show the same trend for both metals: they decrease with temperature. This is in qualitative agreement with the experiment for Sc, except that we do not obtain the maximum at around 30 K. On the other hand, the magnetic susceptibility of yttrium is observed to increase slightly with temperatures below 300 K and to decrease with temperature above 300 K. Our calculated PSS agrees qualitatively with experiment at high temperatures. However, at low temperatures once again, agreement with experiment is not good. Of course, the temperature dependence of the orbital susceptibility should also be estimated, but we think it is likely to be small as in Sc. In order to explain the experimental results it seems that the spin fluctuation effect should be taken into account, which is beyond the scope of the current work. This effect is very important for the temperature dependence of the magnetic properties in these metals [11].

Finally we mention some consequences of these calculations for the study of magnetic transition metal impurities in these metals. Although it is necessary to develop a more exact [24] treatment, we can regard the external field as arising from dilute magnetic transition metal impurities. Our results then suggest that the magnetic moments of such impurities will align with the c-axis. According to the experimental results of Spedding and Croat for Y, an abnormal behaviour for specimens which contained substantial quantities of iron impurities was observed. At low temperatures (<80 K), the values of $\chi_a - \chi_c$ are smaller than those of purer specimens. Our result, namely $\chi_c^{PSS} > \chi_a^{PSS}$, is consistent with this fact. It seems that the orientations of the spins of magnetic iron impurities are indeed along c-axis rather than the a-axis.

Acknowledgment

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