PHYSICAL REVIEW B VOLUME 13, NUMBER 9 1 MAY 1976

Electronic structure and magnetic properties of scandium*

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(Received 19 June 1975)

The Van Vleck orbital and Pauli spin paramagnetic contributions to the magnetic susceptibility of single-crystal and polycrystalline scandium are calculated using the augmented-plane-wave method in conjunction with a linear-combination-of-atomic-orbitals interpolation scheme, which uses s-, p-, and d-type functions in the tight-binding representation. The warped-muffin-tin potential was obtained from overlapping charge densities, which were derived from the atomic configuration $3d^24s$; the exchange interaction was included in full Slater $\rho^{1/3}$ approximation. The Fermi energy is found to lie in a sharp peak in the density-of-states curve. The anisotropy in the magnetic susceptibility and the low-temperature variation of the susceptibility of scandium, particularly the hump around 25°K observed by Spedding and Croat, are successfully explained. The large enhancement of the low-temperature specific heat due to spin fluctuations calculated from the molecular-field parameter in random-phase approximation is shown to account for the absence of superconductivity in scandium.

I. INTRODUCTION

Scandium, having one electron in the $3d$ shell, is the first of the series of transition metals and does not have the unpaired $4f$ electrons unlike other rare earths, to swamp the temperature dependence of magnetic susceptibility χ arising from the Pauli spin paramagnetism and the orbital paramagnetism of d electrons. Therefore, information concerning the electronic structure of Sc in the metallic state and also some of its intermetallic compounds is of fundamental interest for the clarification of the role of d electrons in the transition metals. Although the magnetic susceptibility of scandium has been measured by several groups,[1] neither the value of χ nor its temperature dependence was accurately known until the recent measurements of Spedding and Croat[1] on highly pure Sc were available. These measurements have also shown a previously unobserved maximum around 25 °K in the single-crystal and polycrystalline susceptibility of Sc, which disappears as small amounts of impurities are added. This peak could not be explained, as there is no antiferromagnetic ordering in Sc around that temperature.[2] Although the band structure of scandium has been studied previously,[3-6] to our knowledge, until very recently[5] information on wave functions near the Fermi level, essential to the understanding of these phenomena in Sc, was scarce and incomplete. Based on a tight-binding linear-combination-of-atomic-orbitals (LCAO) scheme,[7] we present here results for the projected and total density of states (DOS), the magnetic susceptibility, and in particular explain the maximum in the χ vs T curve around $T \approx 25$ °K. In Sec. II we discuss the procedural details, and in Sec. III we present the results of our calculations.

II. PROCEDURAL DETAILS

The energy eigenvalues for the high-symmetry points were calculated by using $3d^24s$ atomic configuration[8] with lattice constants[9] appropriate to 11 °K, viz., $a = 6.2391$ a.u. and $c = 9.9316$ a.u. The exchange interaction was included in full Slater $\rho^{1/3}$ approximation. The LCAO interpolation method employed in our calculations consists essentially in assuming a tight-binding LCAO form for the one-electron wave function and parametrizing the Hamiltonian in terms of one- and two-center energy integrals,[10] which are then determined by obtaining the best fit to the augmented-plane-wave (APW) eigenvalues at high-symmetry points in the Brillouin zone. Since scandium has two atoms per unit cell, the electronic structure was adequately represented by 18 basis functions, namely, one s function, three p functions of type x, y, z times $f_1(r)$, and five d functions of type xy, yz, xz, $\frac{1}{2}(x^2-y^2)$, $(3z^2-r^2)/(2/\sqrt{3})$ centered on each atom. In the two-center approximation, the number of independent energy integrals[10] reduces to 16. However, since Sc does not have an ideal hcp structure, 10 additional two-center energy integrals pertaining to the atoms out of basal plane were introduced. These parameters were then varied simultaneously using the techniques discussed by Connolly.[11] The rms error of the fit with 26 parameters for 200 eigenvalues calculated at 21 points in Brillouin zone was 5 mRy.

The quadratic interpolation scheme (QUAD) of Mueller *et al.*[12] was then used to calculate the energy eigenvalues and eigenvectors at a large number of points, to give the histogram representation of projected and total density of states for the energy of interest. To facilitate the application of QUAD scheme to a hcp Brillouin zone, we expanded

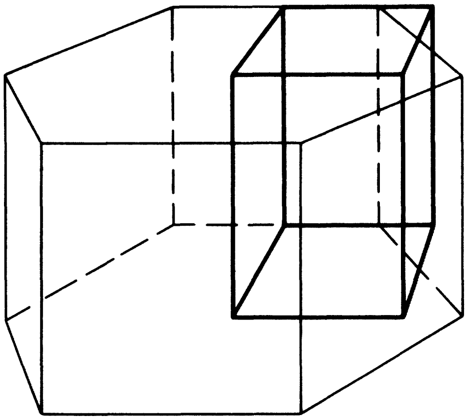

FIG. 1. Orthorhombic sector (represented by heavy lines) of the hcp-structure Brillouin zone used in the QUAD-scheme calculations.

the irreducible wedge of the Brillouin zone to make a bigger orthorhombic sector, as shown in Fig. 1, such that it has also the point-group symmetry of hcp structure. This sector is then divided into small cubes, and the eigenvalues and eigenvectors calculated at 27 points lying at the corners and the centers of faces of each cube are then used to get a quadratic expansion of energy eigenvalues, and eigenvectors in terms of the vector $(\vec{k}-\vec{k}_0)$, $\vec{k}_0$ being the center of the cube. The expansion coefficients are then used in conjunction with the Monte Carlo techniques to calculate the total and projected density of states for various symmetries as follows: We assume that the wave function at the point $\vec{k}$ for the nth band is given by

$$\Psi^n_{\vec{k}}(r)=\sum_p a^n_p(\vec{k})\phi_{p\vec{k}}(\vec{r}), \tag{1}$$

$\phi_{p\vec{k}}(r)$ being the basis function in tight-binding representation for symmetry p, and the sum over p runs over the above-mentioned 18 basis functions. The projected density of states $N_i(E)$ for the symmetry i is given by

$$N_i(E)=\frac{1}{(2\pi)^3}\sum_n\int d\vec{k}\,\delta(E^n_{\vec{k}}-E)\sum_l|a^n_l(\vec{k})|^2, \tag{2}$$

where the summation over l extends over all the basis functions belonging to the symmetry i.

We shall consider now the calculation of the magnetic susceptibility $\chi_{\text{poly}}(T)$ for polycrystalline scandium, and its temperature variation. We have assumed here that the contributions due to all other terms except those due to the exchange-enhanced Pauli spin susceptibility $\chi^e_s(T)$, the Van Vleck orbital susceptibility $\chi_{\text{orb}}(T)$, and the diamagnetic susceptibility χ_{diam} (due to the orbital motion of core and conduction electrons) are negligible. Thus $\chi_{\text{poly}}(T)$ is given by[13]

$$\chi_{\text{poly}}(T)=\chi^e_s(T)+\chi_{\text{orb}}(T)+\chi_{\text{diam}}, \tag{3}$$

where

$$\chi_{\text{orb}}(T)=\tfrac{1}{3}[\chi^c_{\text{VV}}(T)+2\chi^a_{\text{VV}}(T)]$$

and

$$\chi^e_s(T)=\chi_s(T)/[1-\alpha\chi_s(T)]. \tag{4}$$

Here $\chi^c_{\text{VV}}(T)$ and $\chi^a_{\text{VV}}(T)$ are the Van Vleck orbital susceptibility along the c and a crystallographic axes, and $\chi_s(T)$ is the Pauli spin susceptibility. The molecular-field coefficient parameter α proposed by Stoner[14] is related to the Stoner enhancement factor D through the relation

$$D=1/[1-\alpha\chi_s(0)]. \tag{5}$$

The parameter α is in principle a function of temperature, but since we are considering the variation of $\chi_{\text{poly}}(T)$ over a small range of temperature, and the variation of α with temperature is not known, we have assumed it to be independent of temperature, determined from the experimental value of $\chi_{\text{poly}}(T)$ at some temperature T.

The Pauli spin susceptibility is given by[15]

$$\chi_s(T)=\mu^2\frac{\partial}{\partial\zeta}\int_0^\infty\frac{\nu(\epsilon)\,d\epsilon}{1+\exp[(\epsilon-\zeta)/kT]}$$
$$=\frac{\mu^2}{KT}\int_0^\infty\nu(\epsilon)f(\epsilon)[1-f(\epsilon)]d\epsilon, \tag{6}$$

where ζ is the chemical potential, $\nu(\epsilon)$ is the total DOS per atom, $f(\epsilon)$ is the Fermi function, and μ is the Bohr magneton. Owing to the critical position of the Fermi level, we evaluated this integral accurately by interpolating the total DOS between histogram boxes using cubic, quadratic, and linear interpolation methods, and found the same results. We found that the position of the peak in $\chi_s(T)$ is a very sensitive function of Fermi energy and changes by 2 °K if the Fermi level shifts by as little as 0.1 mRy.

The Van Vleck orbital susceptibility χ^c_{VV} and χ^a_{VV} were calculated using the Kubo and Obata[16] formula,

$$\chi^{c(a)}_{\text{VV}}(T)=\mu_B^2\int\frac{d\vec{k}}{(2\pi)^3}\sum_{nn'}\left(\frac{f(E_n(\vec{k}))-f(E_{n'}(\vec{k}))}{E_{n'}(\vec{k})-E_n(\vec{k})}\right)$$
$$\times\langle\psi^n_{\vec{k}}|L_{z(x)}|\psi^{n'}_{\vec{k}}\rangle\langle\psi^{n'}_{\vec{k}}|L_{z(x)}|\psi^n_{\vec{k}}\rangle, \tag{7}$$

where

$$\langle\psi^n_{\vec{k}}|L_z|\psi^{n'}_{\vec{k}}\rangle=\sum_{pp'}a^{n*}_p(k)a^{n'}_{p}(k)\langle\phi_{p\vec{k}}|L_z|\phi_{p'\vec{k}}\rangle, \tag{8}$$

and

$$\langle\psi^n_{\vec{k}}|L_x|\psi^{n'}_{\vec{k}}\rangle=\sum_{pp'}a^{n*}_p(\vec{k})a^{n'}_{p'}(\vec{k})\langle\phi_{p\vec{k}}|\tfrac{1}{2}(L_++L_-)|\phi_{p'\vec{k}}\rangle. \tag{9}$$

The matrix elements of the operators L_x and L_z between various basis functions can be calculated analytically, if one neglects the overlap between the neighboring atoms. In this approximation $\phi_{p\vec{k}}(r)$ becomes independent of $\vec{k}$ and reduces to an atomic orbital function of symmetry p represented by $|p\rangle$ say. We note that the matrix elements involving s functions, or between basis functions of different l symmetry vanish identically. The nonvanishing matrix elements are listed below:

$$\begin{aligned}
&\langle yz|L_z|xz\rangle = -\langle xz|L_z|yz\rangle = i\,,\\
&\langle \tfrac{1}{2}(x^2-y^2)|L_z|xy\rangle = -\langle xy|L_z|\tfrac{1}{2}(x^2-y^2)\rangle = 2i\,,\\
&\langle xz|L_x|xy\rangle = -\langle xy|L_x|xz\rangle = i\,,\\
&\langle \tfrac{1}{2}(x^2-y^2)|L_x|yz\rangle = -\langle yz|L_x|\tfrac{1}{2}(x^2-y^2)\rangle = i\,,\\
&\langle (3z^2-r^2)/2\sqrt{3}|L_x|yz\rangle\\
&\qquad = -\langle yz|L_x|(3z^2-r^2)/2\sqrt{3}\rangle = i\sqrt{3}\,,\\
&\langle z|L_x|y\rangle = -\langle y|L_x|z\rangle = i\,,\\
&\langle y|L_z|x\rangle = -\langle x|L_z|y\rangle = i\,.
\end{aligned} \tag{10}$$

The integrand in the expression for $\chi^a_{\rm vv}$ and $\chi^c_{\rm vv}$ involving the above matrix elements and appropriate energy denominators was exactly computed at 1331 points in the $\frac{1}{8}$ of the Brillouin zone and then the quadratic interpolation scheme,[12] in conjunction with the Monte Carlo sampling techniques, was used to compute the integral. The temperature variation of the orbital susceptibility was calculated using the explicit temperature dependence of the Fermi function. We also calculated $\chi^c_{\rm vv}$ and $\chi^a_{\rm vv}$ without considering the contribution from the basis functions of p ($l=1$) symmetry. We compare our results with those of Ross *et al.*[17] based on the analysis of NMR experiments. In the NMR analysis, the neglect of the p density of states is justified due to the small p hyperfine field relative to that of the s electrons, and to the small p density of states at the Fermi surface relative to that of the d electrons. Thus accordingly we define the fractional s character at the Fermi surface to be

$$\rho_s = \frac{N_s(E_F)}{N_s(E_F)+N_d(E_F)}\,, \tag{11}$$

$N_s(E_F)$ and $N_d(E_F)$ being the projected s and d density of states at the Fermi energy E_F.

We have also calculated the average values of fractional admixture coefficients[17] in the density of states for the symmetries E', A_1', and E'' (alternately denoted by Γ_5, Γ_1, and Γ_6, respectively, in Herring's notation) appearing in the analysis of magnetic susceptibility of Ross *et al.* by calculating the projected density of states for these symmetries.

III. RESULTS

The energy band structure of scandium along high-symmetry directions obtained from the interpolation method using parameters given in Table I is shown in Fig. 2. The solid circles represent the APW eigenvalues. The rms error of the least-square fit is of the order of 5 mRy, and since only the low-lying bands are used to get the best fit to the *ab initio* calculations, the agreement with the interpolation-scheme results is better for low-lying bands. Here the Fermi energy lies in a region where the energy bands are extremely flat, as a result of which the shape of the Fermi surface is highly sensitive to the position of the Fermi energy. This is particularly evident along the AL and HL symmetry directions. The total-density-of-states and d–density-of-states curves shown in Fig. 3 also indicate similar features. The Fermi energy which was obtained by integrating the total-density-of-states curve to yield three electrons per atom, lies exactly in the histogram box of width 1 mRy at a peak in the total- and d - DOS curve. Although the accuracy of band structure calculations is limited to a few millirydbergs, the

TABLE I. Interaction parameters α for scandium in Miasek's (Ref. 10) notation in the two-center approximation. (The nonprimed and the primed parameters pertain to the two atoms in and out of the basal plane, respectively, in a unit cell of the hcp structure.)

Parameter		Rydbergs
s bands	$s0$	0.59696
	$ss\sigma$	−0.03997
	$ss\sigma'$	−0.04534
p bands	$p0$	0.81023
	$pp\sigma$	0.04775
	$pp\sigma'$	0.05928
	$pp\pi$	−0.02626
	$pp\pi'$	−0.03276
d bands	$d0$	0.60140
	$d1$	0.59491
	$d2$	0.60393
	$dd\sigma$	−0.03884
	$dd\sigma'$	−0.04461
	$dd\pi$	0.02705
	$dd\pi'$	0.02961
	$dd\delta$	−0.00614
	$dd\delta'$	−0.00647
sp mixing	$sp\sigma$	0.04604
	$sp\sigma'$	0.05285
sd mixing	$sd\sigma$	0.02931
	$sd\sigma'$	0.03664
pd mixing	$pd0$	−0.01793
	$pd\sigma$	0.03742
	$pd\sigma'$	0.03574
	$pd\pi$	−0.02387
	$pd\pi'$	−0.02526

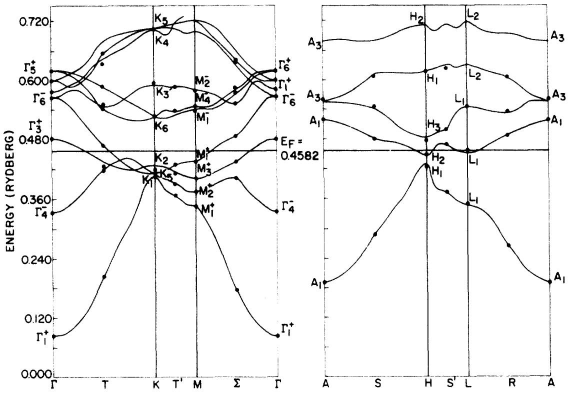

FIG. 2. Energy band structure of scandium from interpolation scheme. The solid circles indicate corresponding APW values.

error in the position of the Fermi level obtained this way can be much smaller by virtue of the very fact that it is so close to the peak. As shown below this critical position of the Fermi energy is responsible for the unusual magnetic properties of scandium. The large value of the fractional d character ρ_d at Fermi energy is in agreement with the experimental data on the magnetic susceptibility and the nuclear magnetic resonance[17] as shown in Table II. However, the projected p density of states at the Fermi energy was found to be about 20% of the total density of states, a rather large quantity. The fractional admixture coefficients $F^{\Gamma(A_1')}$, $F^{\Gamma(E')}$ and $F^{\Gamma(E'')}$ [30.24, 21.2, and 15.2, respectively, in units of $(1-\rho_s)\times 10^2$] at the Fermi energy also differ considerably from their estimated values by Ross *et al.*[17]

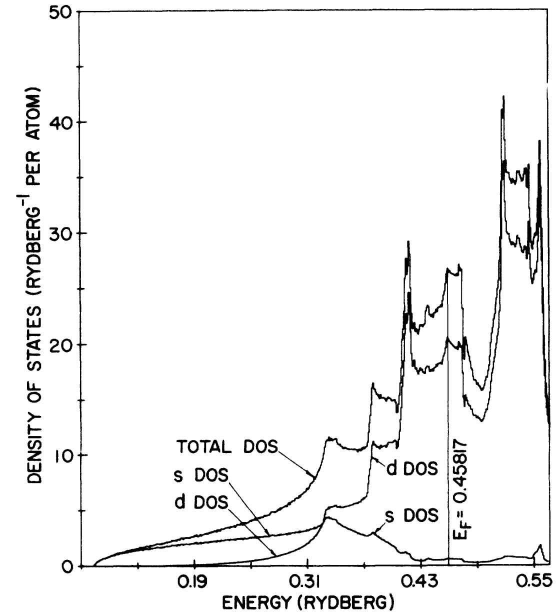

FIG. 3. Total density of states and the projected s and d density of states.

We shall compare now our results for magnetic susceptibility with experiments. The susceptibilities χ_{vv}^{c} and χ_{vv}^{a} calculated using the explicit temperature dependence of the Fermi function were found to be rather insensitive functions of temperature with values of about 2.69×10^{-6} and 2.92×10^{-6} emu/g, respectively. Compared to Spedding and Croat's reported value of $\chi^a - \chi^c \sim 0.42\times 10^{-6}$ emu/g for $T > 1.5$ °K decreasing to $\sim 0.19\times 10^{-6}$ emu/g for $T \sim 60$ °K, we obtain $\chi_{\mathrm{vv}}^{a} - \chi_{\mathrm{vv}}^{c}$ to be about 0.21×10^{-6} emu/g for $T \sim 50$ °K decreasing to 0.21×10^{-6} emu/g for $T \sim 300$ °K. The discrepancy between our calculations and the experimental results for $\chi^a - \chi^c$ could be attributed to additional contributions coming from the anisotropic mass tensor when spin-orbit coupling is considered (which has been neglected in the present study). Of special interest in these calculations is the role of the p character of wave function at the Fermi surface. While the p contribution to the total density of states as mentioned before is about 20%, that to the value of χ_{vv}^{c} or χ_{vv}^{a} individually is about 0.3% and the contribution to the difference $\chi_{\mathrm{vv}}^{c} - \chi_{\mathrm{vv}}^{a}$ is approximately 39%. Another interesting result of our calculations is that the value of $\chi_{\mathrm{vv}}^{a} - \chi_{\mathrm{vv}}^{c}$, calculated using the expression by Ross *et al.*,[17] involving the average values of the fractional admixture coefficients $F^{\Gamma(A_1')}$, $F^{\Gamma(E')}$, and $F^{\Gamma(E'')}$, has not only the wrong magnitude but also the wrong sign. Thus it appears very essential to evaluate the integral for χ_{vv}^{c} and χ_{vv}^{a} exactly. The results for polycrystalline susceptibility $\chi_{\mathrm{poly}}(T)$ assuming α to be independent of temperature, are plotted in Fig. 4 along with the experimental results of Spedding and Croat.[1] Here we assumed $\chi_{\mathrm{diam}} = 0.93\times 10^{-6}$ emu/g, as obtained by Mandelsohn *et al.*,[18] and used Eqs. (3) and (4) with the experimental value of χ_{poly} at 20 °K, to estimate the value of α to be 0.5558×10^{6} g/emu. The position and the height of the peak in $\chi_{\mathrm{poly}}(T)$ is in good agreement with the low-temperature data but at high temperatures $\chi_{\mathrm{poly}}(T)$ is larger than the experimental value, which can be explained by the decrease in the mean molecular-field coefficient parameter α due to increased spin fluctuations at higher temperatures.

Finally we shall consider enhancement of the density of states due to both the electron-phonon interaction and the spin fluctuations, and its relation to the absence of superconductivity in Sc. The enhancement factor λ defined by

$$1+\lambda = N_E/N_B\,, \tag{12}$$

where N_E is the enhanced total DOS and N_B is the

TABLE II. Comparison of present results with other results.

	Present calculation	Ross *et al.*[a]	Other results
$\nu(\epsilon)\,(\mathrm{Ry}^{-1}\,\mathrm{atom}^{-1})$	26.73±0.6	38–57	35.5,[b] 31.0,[c] 17.6,[d] 45.0[e]
$\nu_d(\epsilon)\,(\mathrm{Ry}^{-1}\,\mathrm{atom}^{-1})$	20.58±0.5	...	29.4 ±0.6[b]
$\nu_p(\epsilon)\,(\mathrm{Ry}^{-1}\,\mathrm{atom}^{-1})$	5.54±0.2	...	5.48±0.2[b]
$\nu_s(\epsilon)\,(\mathrm{Ry}^{-1}\,\mathrm{atom}^{-1})$	0.61±0.01	...	0.56±0.05[b]
ρ_s	3.0 ±1.0%	2.4–7.3%	1.9 ±0.2%
ρ_d	97.0 ±1.0%	85–97%	97.0 ±4.0%[b]
$F^{\Gamma(A'_1)}$[i]	30.24	84–92	26.6 ±0.7[b]
$F^{\Gamma(E')}$[i]	21.2	0–4.1	21.3 ±1.3[b]
$F^{\Gamma(E'')}$[i]	15.2	8.8–15.0	14.8 ±0.7[b]
χ^a_{vv} (11) (10^6 emu/g)	2.92	...	2.88[h]
χ^c_{vv} (11) (10^6 emu/g)	2.69	...	2.74[h]
χ^a_{vv} (11) $-\chi^c$ (11) (emu/g)	0.23	0.25	0.14,[h] 0.28[g]
χ_{orb} (11) emu/g	2.84	0.17	2.83,[h] 2.22[f]
χ_s (11) emu/g	1.41	...	...
χ^e_s (11) emu/g	6.52	...	...
χ_{poly} (11) emu/g	8.47	8.23	8.45
$\alpha\times 10^{-6}$ g/emu	0.5558	...	...
$D=1/[1-\alpha\chi_s(20)]$	4.6	3.5	...
$\bar{I}=\frac{1}{2}\alpha\chi_s(0)$	0.393	...	...

[a] See Ref. 17.
[b] See Ref. 5.
[c] See Ref. 4.
[d] See Ref. 3.
[e] See Ref. 19.
[f] See Ref. 21.
[g] See Ref. 1.
[h] The p character of wave function is neglected here.
[i] These are average fractional admixture coefficients in units of $(1-\rho_s)\times 10^{-2}$ and are defined in Ref. 17.

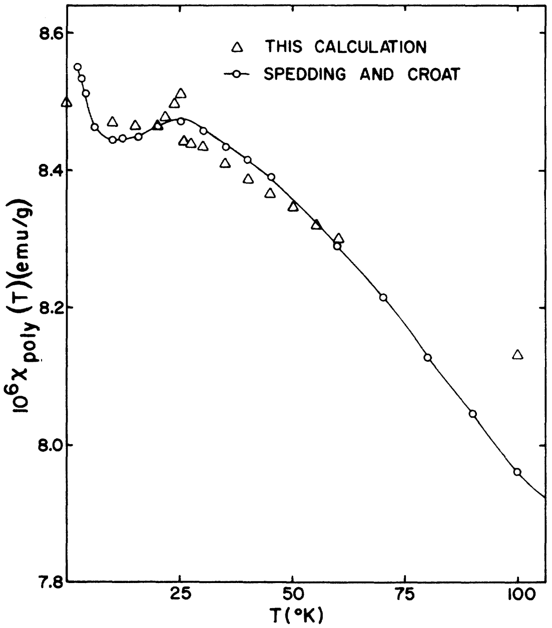

FIG. 4. The variation of magnetic susceptibility of polycrystalline Sc with temperature. For comparison the results of Spedding and Croat on polycrystalline sample 4-155(poly) are plotted.

bare DOS, can be written as

$$\lambda = \lambda_{ep} + \lambda_{ee} + \lambda_{\mathrm{spin}}\ , \tag{13}$$

where λ_{ep} is the enhancement factor due to the electron-phonon interaction and is responsible for the superconducting properties of materials. λ_{spin} is the contribution due to the spin fluctuations or the electron-paramagnon interaction, and λ_{ee} is due to the electron-electron interaction. Generally λ_{ee} is very small compared to λ_{ep} and λ_{spin} for transition metals. The total density of states N_B obtained from our band-structure calculations is 26.73 Ry^{-1} atom^{-1}. The enhanced density of states[19] N_E obtained from the electronic specific-heat coefficient $\gamma(0)$ at 0 K, is 60.2 Ry^{-1} atom^{-1}. Thus the enhancement factor λ from our calculations is about 1.25. The enhancement factor due to the electron-phonon interaction λ_{ep}, estimated using the value of density of states $N_B(\approx 45.0\ \mathrm{Ry}^{-1}\ \mathrm{atom}^{-1})$ obtained from the extrapolation of the electronic specific-heat coefficient $\gamma(T)$ at high temperatures to 0 K is about 0.3. This value of λ_{ep} when substituted in the McMillan's equation for T_c, the superconducting transition temperature, gives $T_c = 0.005$ K and is thus consistent with the observed absence of superconductivity in scandium. This shows that the virtual scattering of electrons on the Fermi surface via spin fluctuations plays a very dominant role in enhancing the density of states in addition to that due to the electron-phonon interaction for Sc. In fact, the value of λ_{sp} (≈ 1.24) obtained from the relation[20] $\lambda_{sp} = 4.5 \ln(1 - \bar{I}) - 1$, where $\bar{I} = \frac{1}{2}\alpha\chi_s(0)$, with our estimated value of $\alpha = 0.5558 \times 10^6$ emu/g and $\chi_s(0) = 1.4138 \times 10^{-6}$ g/emu, shows that almost all the observed enhancement of the density of states in low-temperature specific-heat measurements is due to the spin fluctuations, and λ_{ep} is indeed very small.

The main conclusion from these calculations is that the peak in the susceptibility of scandium can be explained successfully only if we assume that the Fermi level Sc is trapped within a sharp peak in the density-of-states curve. The value of the Pauli spin susceptibility derived from the itinerant electron model and the molecular-field parameter α estimated from the magnetic susceptibility measurements can explain the observed absence of superconductivity in scandium. The calculated anisotropy in the susceptibility measurements, the projected density of states are also consistent with the experiments. Thus one can safely believe in the itinerant character of *d* electrons in transition metals.

ACKNOWLEDGMENTS

I am highly indebted to Professor S. K. Sinha for many enlightening discussions and guidance. I would like to thank Professor A. J. Freeman for supplying the augmented-plane-wave computer program and to Dr. M. H. Mueller for supplying the lattice constants.

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*Based on work performed under the auspices of the U.S. Energy Research and Development Administration.

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