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Susceptibilities of $SmPd_2Al_3$ and $SmPd_2Ga_3$ studied with a crystal-field model and an *ab initio* approach

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A general formula for the susceptibility of rare-earth compounds was derived with perturbation theory and mean-field approximation. During the formulation all relevant interactions, including *L*-*S* coupling, Ruderman-Kittel-Kasuya-Yosida exchange, crystal-field splitting, as well as the influence of conduction-electron polarization and *J* mixing, were considered. In order to verify the correctness of the formula, *ab initio* calculations were performed to obtain the crystal-field parameters (CFP's) of $SmPd_2Al_3$ and $SmPd_2Ga_3$ with a recently developed self-interaction-correction approach. The magnetic susceptibilities of the samarium compounds calculated with the formula and the CFP's exhibit very good similarity to the experimental results in the paramagnetic region.

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I. INTRODUCTION

In samarium intermetallic compounds, the energy separation between the ground ($J=\frac{5}{2}$) and the first-excited ($J=\frac{7}{2}$) multiplets is only 1400 K, thus in comparison with other rare-earth compounds, the temperature-independent Van-Vleck term of Sm compounds is expected to contribute more substantially to magnetic susceptibility. Moreover, since the g_J factor of the ground multiplet is only $\frac{7}{2}$, the Curie part of the susceptibility is relatively much smaller than in other rare-earth compounds. Therefore one has to consider the admixture of the excited *J* multiplet to the ground *J* multiplet and the transition between them when dealing with the magnetic and thermodynamic properties of such complicated systems.

de Wijn *et al.*[1] has derived a formula to calculate the susceptibility of samarium compound, where the f-f exchange interaction between the neighboring magnetic ions was treated as a perturbation to the crystal-field interaction and *L*-*S* coupling. With the inclusion of all matrix elements within and between at least three lowest *J* multiplets i.e., $J=\frac{5}{2}$, $J=\frac{7}{2}$, and $J=\frac{9}{2}$, the model calculations were compared with the measured magnetic susceptibilities for the ferromagnetic $SmAl_2$ ($T_C=120$ K) and the antiferromagnetic $SmSn_3$ ($T_N=11$ K).

In a metal that contains the tripositive samarium ion, the influence of the conduction-electron polarization upon the magnetic susceptibility of the metal is sometimes very much greater than in other normal rare-earths compounds. A theory of the susceptibility of metallic samarium materials was introduced by Stewart.[2] In his work, he considered above-mentioned polarization effect besides the interionic Heisenberg exchange couplings, and the admixture of the $J=\frac{7}{2}$ state into the $J=\frac{5}{2}$ ground state, but unfortunately neglected crystal-field split in each *J* multiplet, which actually has significant influence on the magnetic behaviors of the systems and cannot be simply omitted. The susceptibility was found in the theory to be of the simple form $\chi=\chi_0+D/(T-\theta)$, and the expression was used to fit the experimental data for the susceptibility of double-hexagonal-close-packed (dhcp) structure samarium to an accuracy of 0.01 in the temperature region 110–230 K, and the parameters extracted from the fit, e.g., $J(0)\rho(E_F)=0.100$ for dhcp samarium metals, were in agreement with those obtained for other light rare-earth metals. Another expression was also derived for the susceptibilities of the metals containing normal rare earths, in which both the influences, conduction-electron polarization as well as the crystal-field interaction were considered,

$$\chi=\frac{\chi_c[1+2J(0)\rho(E_F)(g_J-1)/g_J]^2}{1-\lambda\chi_c}+\chi_M, \tag{1}$$

where λ is the molecular-field constant and χ_M the matrix susceptibility, that is, the sum of the Pauli, Landau, and core diamagnetic contributions. According to Eq. (2-20) of Ref. 2,

$$\frac{\langle S_z\rangle}{\langle L_z+2S_z\rangle}=\frac{g_J-1}{g_J}. \tag{2}$$

Based on the theory of Stewart described above, the ratio of (g_J-1) to g_J in expression (2) was substituted into Eq. (1) by Zhou *et al.*[3] in order to account for the effects of crystal-field splitting and conduction-electron polarization (CEP) in samarium compounds whereas omitting the last term in Eq. (1). The formula, obtained in such simplified approximation for the susceptibility, was used to fit the experimental data for $SmRh_4B_4$. Good agreement, as they claimed, was achieved that gave $2J(0)\rho(E_F)=0.064$. This result is significantly larger than the value obtained by Stewart from an analysis of the polycrystalline data, where the effects of crystal-field splitting were actually neglected as pointed previously in this section.[4]

In present work, a more general formula, to be explained in details in the following section, for calculating the susceptibility of samarium compounds was derived with perturbation theory. In the procedure of the derivation, we treated the effects of the interionic Heisenberg exchange couplings and the conduction-electron polarization as perturbations to the crystal-field interaction and the *L*-*S* coupling. In order to test and apply our theory, we performed *ab initio* calculations for two samarium compounds $SmPd_2Al_3$ and $SmPd_2Ga_3$ to obtain their crystal-field parameters with a self-interaction-correction (SIC) technique,[5] which mimics the first Hund's Rule and will be explained briefly in Sec. III. Considering the admixture of the excited $J=\frac{7}{2}$ and $J=\frac{9}{2}$ states into the $J=\frac{5}{2}$ ground state and also the crystal-field splitting of the multiplets, model calculations of the susceptibilities are presented and compared with the experimental results[6–8] in Sec. IV.

II. FORMULATING THE SUSCEPTIBILITY WITH PERTURBATION THEORY

In the compounds under consideration, Sm can be assumed in the stable 3+ local state, that is, a local open $(4f)^5$ shell is to be treated. The relevant Hamiltonian is

$$\mathcal{H}=\lambda\vec{L}\cdot\vec{S}+\mathcal{H}_{CF}+\mathcal{H}_{Zeem}+\mathcal{H}_{ex}+\mathcal{H}_{s-f}. \tag{3}$$

We know that the first spin-orbit coupling term is (J,M) diagonal, and the coupling constant is $\lambda\approx410$ K. Hence the ${}^6H_{7/2}$ and ${}^6H_{9/2}$ multiplets are only 1400 K and 3200 K above the ground-state multiplet, respectively. Therefore, the crystal-field Hamiltonian $\mathcal{H}_{CF}$ is expressed in the general tensor-operator representation by Racah[9]

$$\mathcal{H}_{CF}=\sum_{k,q}N_k^qA_k^q\langle r^k\rangle U_q^k, \tag{4}$$

where N_k^q is the normalization factor tabulated by Weber and Bierig,[10] A_k^q is the usual crystal-field parameters (CFP's), and U_q^k, the spherical unit tensor operator, is defined by

$$U_q^k=\left(\frac{4\pi}{2k+1}\right)^{1/2}Y_k^q. \tag{5}$$

$SmPd_2Al_3$ and $SmPd_2Ga_3$ have hexagonal point symmetry of the Sm site, hence

$$\mathcal{H}_{CF}=N_2^0A_2^0\langle r^2\rangle U_0^2+N_4^0A_4^0\langle r^4\rangle U_0^4+N_6^0A_6^0\langle r^6\rangle U_0^6+N_6^6A_6^6\langle r^6\rangle U_6^6. \tag{6}$$

The Zeeman term of Eq. (3) describes the direct coupling of the $4f$ shell to an external magnetic field $\vec{H}$:

$$\mathcal{H}_{Zeem}=\mu_B\vec{H}\cdot(\vec{L}+2\vec{S}). \tag{7}$$

The term $\mathcal{H}_{ex}$ describes the interionic Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction of $4f$ shells via a transformed exchange field $\vec{H}_{ex}$,

$$\mathcal{H}_{ex}=2\mu_B\vec{H}_{ex}\cdot\vec{S}. \tag{8}$$

And finally, the last term of Eq. (3) represents the effect of conduction-electron polarization due to an applied field $\vec{H}$ and acting on the $4f$ shell. It is expressed by

$$\mathcal{H}_{s-f}=2\mu_BJ(0)\rho(E_F)\vec{H}\cdot\vec{S}, \tag{9}$$

where $\rho(E_F)$ is the conduction-electron density of states at the Fermi level and for one spin direction so that $2\mu_B\rho(E_F)\vec{H}$ is the Pauli paramagnetic spin density, and $J(0)$ is the $\vec{q}=0$ component of the s-f coupling constant.

Anticipating a paramagnetic situation with $\vec{H}_{ex}\propto\vec{H}$, we split the Hamiltonian Eq. (3) into its field-independent and field-dependent parts:

$$\mathcal{H}=\mathcal{H}^0+\mathcal{H}', \tag{10}$$

$$\mathcal{H}^0=\lambda\vec{L}\cdot\vec{S}+\mathcal{H}_{CF}, \tag{11}$$

$$\mathcal{H}'=\mu_BH(L_z+2S_z)+2\mu_BH_{ex}S_z+2\mu_BHJ(0)\rho(E_F)S_z. \tag{12}$$

Denoting by $|m\rangle,E_m^{(0)}$ the eigenstate and energy of $\mathcal{H}^0$, and calculating the energy perturbations in first order in H, we find for the thermal average of the spin and orbital polarization the Curie and Van-Vleck contributions:

$$\langle S_z\rangle=\mu_BH\sigma_{L+2S,S}+2\mu_BH_{ex}\sigma_{S,S}+2\mu_BHJ(0)\rho(E_F)\sigma_{S,S}, \tag{13}$$

$$\langle L_z+2S_z\rangle=\mu_BH\sigma_{L+2S,L+2S}+2\mu_BH_{ex}\sigma_{S,L+2S}+2\mu_BHJ(0)\rho(E_F)\sigma_{S,L+2S}, \tag{14}$$

where

$$\sigma_{A,B}=\sum_m\left(-\frac{\langle m|A_z|m\rangle\langle m|B_z|m\rangle}{kT}+2\sum_{m'\neq m}\frac{\langle m|A_z|m'\rangle\langle m'|B_z|m\rangle}{E_m^{(0)}-E_{m'}^{(0)}}\right)p_m^{(0)}, \tag{15}$$

with $p_m^{(0)}=\exp(-E_m^{(0)}/kT)/Z$, here Z is the unperturbed partition function. The transformed exchange field H_{ex} may be eliminated by substituting

$$2\mu_BH_{ex}=-\mathcal{J}_{ff}\langle S_z\rangle, \tag{16}$$

into Eq. (13) with the result

$$\frac{\langle S_z\rangle}{\mu_BH}=\frac{\sigma_{L+2S,S}+2J(0)\rho(E_F)\sigma_{S,S}}{1+\mathcal{J}_{ff}\sigma_{S,S}}, \tag{17}$$

which is proportional to the excess Knight shift, and

$$\frac{\langle L_z+2S_z\rangle}{\mu_BH}=\sigma_{L+2S,L+2S}+2J(0)\rho(E_F)\sigma_{S,L+2S}-\mathcal{J}_{ff}\sigma_{L+2S,S}\frac{\sigma_{L+2S,S}+2J(0)\rho(E_F)\sigma_{S,S}}{1+\mathcal{J}_{ff}\sigma_{S,S}}, \tag{18}$$

which is proportional to the susceptibility of a bare magnetic ion.

Be aware that in external field the overall magnetic moment considered is contributed by the magnetic rare-earth ion and the conduction electrons. Equation (18) only accounts for the first part. We know that the magnetization per ion of the electron gas is proportional to the spin momentum of the ion according to Ref. 2

$$m^{(e)} = -2\mu_B J(0)\rho(E_F)\langle S^z\rangle, \tag{19}$$

that is,

$$\langle s^{(e)}\rangle = J(0)\rho(E_F)\mu_B H \frac{\sigma_{L+2S,S} + 2J(0)\rho(E_F)\sigma_{S,S}}{1+\mathcal{J}_{ff}\sigma_{S,S}}. \tag{20}$$

Therefore, to include the contribution of the conduction electrons, the factor $-\mathcal{J}_{ff}\sigma_{L+2S,S}$ in the third term of Eq. (18) should be replaced by

$$\mathcal{A}(T) = -\mathcal{J}_{ff}\sigma_{L+2S,S} + 2J(0)\rho(E_F). \tag{21}$$

If the effects of conduction-electron polarization are omitted, simply setting $J(0)\rho(E_F)=0$ in Eqs. (18) and (21), we obtain the same formula as derived by de Wijn.[1] This verifies the correctness of the presently derived expressions, and means that the current model is an extension of de Wijn's.

III. SIC–LOCAL DENSITY APPROXIMATION CALCULATIONS OF THE CRYSTAL FIELD PARAMETERS FOR THE LOCALIZED AND POLARIZED SHELL [5]

SmPd$_2$Al$_3$ and SmPd$_2$Ga$_3$ crystallize in hexagonal structure, in which Sm and Pd atoms are on the same layers, alternating along the c direction with layers of pure Al or Ga atoms.[6–8] The lattice constants, $a=5.4131$ Å, 5.3950 Å, $c=4.1997$ Å and 4.2430 Å for these two compounds respectively, were used in present calculations.

The $4f$ electrons are assumed localized, and the converged anisotropic distribution of the charge density obtained by local-density-approximation (LDA) calculations was used to derive the crystal-field parameters $A_l^{m's}$, of which the analytic expression in terms of the radial $4f$ wave function and effective potential formed by the surrounding ions and conduction electrons was given in our previous paper.[5] Care must be taken to treat the functions of $4f$ electrons since the calculated CFP's are very sensitive to the charge distribution of the incompletely filled shell. Self-interaction-corrected–local-spin-density approximation (SIC-LSDA)(Ref. 11) that removes the spurious self-interaction present in LSDA of the Kohn-Sham orbits can provide a reasonable asymptotic behavior of the radial wave function to be used for the calculations of crystal-field parameters. Explicitly, if the correction is introduced, Kohn-Sham equation takes the form[11]

$$\left[-\frac{\nabla^2}{2} + v(\vec{r}) + v_H(\vec{r}) + v_{XC}^{\mu\sigma}(\vec{r})\right]\phi_{\mu\sigma}(\vec{r}) = \varepsilon_{\mu\sigma}\phi_{\mu\sigma}(\vec{r}), \tag{22}$$

where

$$v_{XC}^{\mu\sigma}(\vec{r}) = v_{XC}^{LSDA}(n_\uparrow, n_\downarrow, \vec{r}) - \int d^3r' \frac{|\phi_{\mu\sigma}(\vec{r}\,')|^2}{|\vec{r}-\vec{r}\,'|} - v_{XC}^{LSDA}(|\phi_{\mu\sigma}(\vec{r})|^2, 0, \vec{r}), \tag{23}$$

σ denotes the spin of the electron and $v_{XC}^{LSDA}(n_\uparrow, n_\downarrow, \vec{r})$ is the exchange and correlation potential at $\vec{r}$, where electron densities for spin up and spin down are $n_\uparrow$ and $n_\downarrow$, respectively.

TABLE I. Calculated crystal-field parameters.

Compounds	$A_2^0\langle r^2\rangle$ (K)	$A_4^0\langle r^4\rangle$(K)	$A_6^0\langle r^6\rangle$(K)	$A_6^6\langle r^6\rangle$(K)
SmPd$_2$Al$_3$	-549.02	74.88	5.51	-210.07
SmPd$_2$Ga$_3$	-800.06	81.21	6.89	-203.13

According to the first Hund's Rule, since the $4f$ shell of Sm is less than half filled, all the $4f$ electrons are polarized along one direction. This rule has been implemented in the linear-combination-of-atomic-orbitals program by taking above assumption into account when $v_{XC}^{\mu\sigma}(\vec{r})$ is calculated. The technique, described in more details in our previous paper,[5] indeed facilitates the localization of $4f$ electrons—all r moments, especially $\langle r^6\rangle$, are reduced considerably.

IV. RESULTS AND DISCUSSIONS

With the lattice constants of the crystals fed to the program and by applying the SIC-LSDA technique described in previous section, we obtained the CFP's for the two substances as tabulated in Table I, and consequently the crystal-field levels and their eigenvalues. The CFP's of the two compounds have the same magnitude and sign as the corresponding ones obtained previously for NdPd$_2$Al$_3$ and NdPd$_2$Ga$_3$ with the same approach,[5] thereby in good agreement with those measured by Dönni *et al.* with neutron scattering.[12,13] The crystal-field induced levels of the two compounds are doubly degenerate, of which the three lowest doublets account mainly for $J=\frac{5}{2}$, the next four lowest doublets are associated with $J=\frac{7}{2}$, and the five highest doublets attributed to $J=\frac{9}{2}$ as the coefficients of the eigenfunctions show. In the case of SmPd$_2$Al$_3$, two levels of $J=\frac{9}{2}$, $|\frac{9}{2},\pm\frac{7}{2}\rangle$ and $|\frac{9}{2},\mp\frac{5}{2}\rangle$, and two of $J=\frac{7}{2}$, $|\frac{7}{2},\pm\frac{7}{2}\rangle$ and $|\frac{7}{2},\mp\frac{5}{2}\rangle$, are mixed to the lowest doublet; each of $J=\frac{7}{2}$ and $J=\frac{5}{2}$, $|\frac{7}{2},\mp\frac{1}{2}\rangle$ and $|\frac{5}{2},\mp\frac{1}{2}\rangle$, are mixed to the highest doublet, etc. Such mixing between different J levels is essential to explain the main features of the magnetic properties of Sm compounds.

To calculate the paramagnetic susceptibilities for the two compounds with the formulas derived in present work, we still need other two parameters: $J(0)\rho(E_F)$, which measures the coupling strength between the conduction electrons and the localized rare-earth ions, and $\mathcal{J}_{ff}$, the RKKY exchange constant. The first one can be easily obtained by *ab initio* calculation based on Eq. (19). That is, polarizing the conduction electron bands to calculate the induced magnetic moment of a rare-earth ion, or vice versa, the proportional factor in the expression provides the parameter we need. In this way we obtained $J(0)\rho(E_F)=0.019$ for SmPd$_2$Al$_3$ and

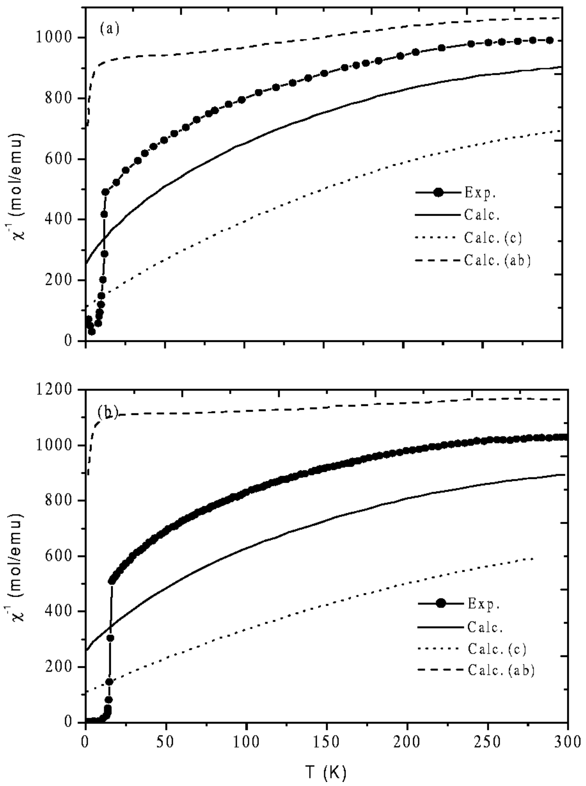

FIG. 1. Comparisons between calculated reciprocal susceptibilities and experimental results for (a) $SmPd_2Al_3$ and (b) $SmPd_2Ga_3$. The calculated two components χ_c and χ_{ab} are also displayed in the figure.

0.014 for $SmPd_2Ga_3$, respectively, very close to the corresponding parameters 0.026 and 0.020 of the isostructural compounds $NdPd_2Al_3$ and $NdPd_2Ga_3$ computed with the same approach.[5] As to the second parameter $\mathcal{J}_{ff}$, we can obtain it simply by varying the parameter to select the one that produces the best similarity to the experimental curve, since as observed the overall susceptibility, calculated with formula $\chi=\frac{1}{3}(2\chi_{\perp}+\chi_{\parallel})$, is very sensitive to the change of the parameter in a relative narrow range. The exchange-coupling constants determined in such way are -10.9 K for the first compound and -15.3 for the second one. Figures 1(a) and 1(b) display the reciprocal susceptibilities of the two compounds plotted with above two sets parameters and the corresponding experimental curves. For the completeness, besides the overall averaged reciprocal susceptibilities, which are needed for direct comparison with the experimentally measured data, we also depicted the theoretical components along c axis and in ab plane. Indeed, the compounds are of very strong anisotropic magnetic property, and the theoretical curves exhibit very good similarities to the experimental ones except the systematically smaller magnitude in whole paramagnetic temperature region. Below transition temperatures, 12 K of $SmPd_2Al_3$ and 17 K of $SmPd_2Ga_3$, the first compound is believed antiferromagnetically ordered, and at least two magnetic transitions were observed;[6] the second one exhibits complex magnetic structure that has not yet been resolved.[8] As expected, in this temperature region the exchange interaction becomes comparable to or stronger than the crystal-field interaction and this term in the Hamiltonian cannot be treated as perturbation, therefore the susceptibility formulas derived in this paper cannot be applied in the ordered phase.

Zhou *et al.*[3] have studied the anisotropic magnetic properties of single crystal of $SmRh_4B_4$. To take account of a possible misalignment of the sample, particularly for the hard axis, due to a tendency of the sample to rotate in the magnetometer toward the easy axis, and especially the nonmagnetic impurity phases present in the sample, they multiplied the calculated results for both components by a factor of 1.36 and achieved very good representation of the experimental data. If we also take account of the effects of such possibly existing impurities and multiply our data with a factor of 1.1–1.2, we will achieve a very good reproduction of the experimental results.

The exchange-coupling constants, which produce best fittings, are very close to (for the first compound) or the same as (for the second compound) the corresponding values of the isostructural compounds $NdPd_2Al_3$ and $NdPd_2Ga_3$, respectively, obtained for the two systems by fitting the specific heats with the crystal-field plus mean-field model.[5] Above fact is by no means an accidental accordance. We know that the famous de Gennes rule is usually used to determine the transition temperatures of one series of rare-earth systems once the transition temperature of a special compound of them is known, this implies that the exchange-coupling constants $\mathcal{J}_{ff}$ can approximately be taken as same for the whole series. Due to crystal-field interaction, the variation of the transition temperatures with R in one series may not follow the de Gennes rule, but as treated by Dunlap *et al.*,[14] the exchange constant, λ_0 in their paper, can still be treated approximately same for the whole series, and the modified de Gennes rule with such approximation indeed well predicted the transition temperatures of $R\mathrm{Rh}_4\mathrm{B}_4$ series.

The physical essence behind this phenomena may be explained by the theory of electronic structure. In the rare-earth (R) transition-metal (T) intermetallics, the exchange path between rare-earth ions can be described as $4f$-$5d$-$5d$-$4f$, that is, the $4f$ electron spins induce a local $5d$ spin moment through the intra-atomic $4f$-$5d$ exchange with subsequent direct $5d$-nd spin moment interaction with any other neigh-

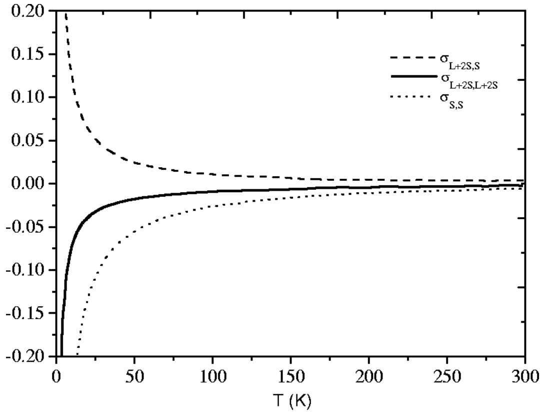

FIG. 2. The temperature dependence of $\sigma_{L+2S,L+2S}$, $\sigma_{L+2S,S}$ and $\sigma_{S,S}$ for $SmPd_2Al_3$.

TABLE II. $\sigma_{L+2S,L+2S}$, $\sigma_{L+2S,S}$, $\sigma_{S,S}$ and their contributions to the susceptibility of $\mathrm{SmPd_2Al_3}$.

	$\sigma_{L+2S,L+2S}$ (1/K)	$\sigma_{L+2S,S}$ (1/K)	$\sigma_{S,S}$ (1/K)	Second term (1/K)	Third term (1/K)	$\mathcal{A}(T)$
1 K	−0.748	1.411	−2.673	0.056 44	0.6654	14.150
10 K	−0.076	0.140	−0.269	5.6×10^{-3}	0.05043	1.440
50 K	−0.0162	0.0267	−0.0542	1.068×10^{-3}	4.884×10^{-3}	0.3067
100 K	−0.008 63	0.0116	−0.0257	4.64×10^{-4}	1.312×10^{-3}	0.1560
150 K	−0.006 11	0.006 37	−0.0161	2.548×10^{-4}	5.114×10^{-4}	0.1037
200 K	−0.004 93	0.003 82	−0.0115	1.528×10^{-4}	2.357×10^{-4}	0.078 20
250 K	−0.004 30	0.002 37	−0.009 04	9.48×10^{-5}	1.173×10^{-4}	0.063 70
300 K	−0.003 95	0.001 46	−0.007 48	5.84×10^{-5}	5.8970×10^{-5}	0.0560

boring nd spin moment on another rare-earth site, certainly mixed with $4f$-$6s$-$6s$-$4f$ and $4f$-$6p$-$6p$-$4f$ according to the Campbell model.[15] In a given series of rare-earth transition-metal compounds where R is varying and T is fixed, the direct $5d$-nd exchange interaction remains roughly constant.[16] Thus, any variation of R-R interactions across the series is mainly determined by the intra-atomic exchange integrals of the R atoms. Actually, calculations with Hartree-Fock approximation and LSDA have shown that such exchange integrals $\mathcal{J}_{f-s}$, $\mathcal{J}_{f-p}$ and $\mathcal{J}_{f-d}$ decreases slightly with the number increment of $4f$ electrons.[17]

In order to understand the magnetic behavior of the compound, $\sigma_{L+2S,L+2S}$, $\sigma_{L+2S,S}$, and $\sigma_{S,S}$ for $\mathrm{SmPd_2Al_3}$ are depicted according to Eq. (15) in Fig. 2 within the temperature domain $0\sim300$ K, and the values of them, the second and the third terms of Eq. (18) at 1 K, 10 K, 50 K, . . . are tabulated in Table II. $\mathcal{A}(T)$, which describes the joint effects of the exchange coupling between the magnetic samarium ions and the polarization of the conduction electrons, is also listed in the table. In the temperature region below 100 K, $\mathcal{A}(T)\gg2J(0)\rho(E_F)\approx0.04$, meaning that the effect of molecular-field interaction is much stronger than that of conduction-electron polarization. But, when the temperature increases, $\mathcal{A}(T)\sim0.04$, meaning that the effect of conduction-electron polarization becomes dominating, or comparable with that of molecular-field interaction. In Fig. 2, $\sigma_{L+2S,L+2S}$ and $\sigma_{S,S}$ are negative, but $\sigma_{L+2S,S}$ is positive. Since $J(0)\rho(E_F)$ and the denominator of the third term of Eq. (18) are all positive, their products with $\sigma_{L+2S,S}$ are positive, differing from $\sigma_{L+2S,L+2S}$, the main contribution of the magnetic ion to the susceptibility. Therefore, the effects of the conduction-electron polarization are expected to reduce the susceptibility, increasing $J(0)\rho(E_F)$ will cause the reduction of the susceptibility. Also, since $-\mathcal{J}_{ff}\sigma_{L+2S,S}$ is positive if the coupling between the neighboring ions is antiferromagnetic, its product with $\sigma_{L+2S,S}$ and the denominator is also positive in the whole temperature domain either, enhancing such coupling is expected to offset the effect of external field.

V. CONCLUSIONS

The SIC-LSDA technique developed recently helps to produce reasonable crystal-field parameters for describing the magnetic and thermodynamic properties of rare-earth compounds. The magnetic susceptibilities calculated with the formulas, as far as we know derived for the first time with perturbation theory and mean-field approximation in the frame of a crystal-field model, exhibit good similarity to the experimental results, demonstrating the essential roles of RKKY exchange interaction, conduction-electron polarization, as well as the strong influence of J mixing in samarium compounds. In the whole paramagnetic phase, the measured and the calculated average susceptibilities, as well as the two computed components perpendicular and parallel to c axis, are of very similar features for the two compounds. It is easy to understand since the atoms Al and Ga possess similar electronic structure except the spatial distribution of the valence electrons of Ga is somehow more extensive than Al in the crystals.

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