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We present results of theoretical and experimental studies of the electronic structure and magnetic properties of \( \text{RT}_4\text{Al}_8 \) systems. The electron spectrum and field induced magnetic moment, as well as their dependencies on the unit cell volume, are calculated for the paramagnetic phase of the \( \text{RT}_4\text{Al}_8 \) systems. The calculations are supplemented by measurements of the magnetic susceptibility of representative \( \text{RT}_4\text{Al}_8 \) compounds as a function of temperature and hydrostatic pressure. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4954784]

1. Introduction

\( \text{RT}_4\text{Al}_8 \) compounds (where \( R \) is a rare earth element and \( T = \text{Fe}, \text{Mn}, \text{Cr} \)) crystallize into a tetragonal crystal structure of the type \( \text{ThMn}_{12} \) (Fig. 1) and have a great variety of magnetic properties.\(^{1-5}\) This variety shows up most clearly in the compounds with \( T = \text{Fe} \), where the iron sublattice becomes ordered at 100–150 K when the temperature is lowered, while magnetic ordering in the \( R \) sublattice occurs at 10–30 K.\(^3\) Both transitions are antiferromagnetic (AFM) in most cases and are characterized by a complicated magnetic structure.\(^{6-9}\)

The existence of two magnetic subsystems makes it possible to study the hierarchy of Fe-Fe, R-R, and R-Fe exchange interactions, which is of interest for the fundamental physics of magnetic phenomena and for the creation of hard magnetic materials with a high iron content.\(^5\)

The properties of the \( \text{RT}_4\text{Al}_8 \) compounds with a nonmagnetic element \( R \) from the lanthanum group (\( R = \text{Sc}, \text{Y}, \text{La}, \text{Lu} \)) are determined predominantly by the \( 3d \)-sublattice of the metal. The weak dependence of the magnetic properties on the element \( R \) shows up most clearly in the \( \text{RFe}_4\text{Al}_8 \) compounds; this is explained by the dominant contribution of the \( 3d \)-states of the iron atoms to their magnetism. In this case, the magnetic susceptibility as a function of temperature, \( \chi(T) \), has a distinct maximum near the magnetic ordering temperature and it does not obey the Curie-Weiss law in the paramagnetic region.

Another feature of the \( \text{RFe}_4\text{Al}_8 \) family is the detection of traces of a superconducting phase in the compounds \( \text{ScFe}_4\text{Al}_8(T_c = 6 K) \), \( \text{YFe}_4\text{Al}_8(T_c = 6 K) \), and \( \text{LuFe}_4\text{Al}_8(T_c \sim 24 K) \) in studies of their surface resistivity and specific heat,\(^{10,11}\) well as in \( \text{YFe}_4\text{Al}_8 \) based on magnetization data.\(^12\) Although there is no generally accepted point of view regarding this question,\(^13\) further study may be useful for understanding the relationship between superconductivity and the magnetic state of these kinds of compounds.

The large spread in published data on the magnetic properties of \( \text{RFe}_4\text{Al}_8 \) compounds is noteworthy and may be a consequence of the different techniques used to prepare the samples and of the high sensitivity of their characteristics to deviations from stoichiometry. More unique information on the magnetic properties has been obtained for \( \text{RMe}_4\text{Al}_8 \) compounds with nonmagnetic elements \( R \).\(^{14,15}\) Magnetic ordering has not been observed in this system and the maxima in the \( \chi(T) \) curves observed at high temperatures (200–400 K) are apparently caused by the character of the band structure. The distinctive feature of the \( \text{RMn}_4\text{Al}_8 \) compounds is the significant influence of chemical pressure effects on their magnetism, as confirmed by an anomalously high dependence of the magnetic susceptibility \( \text{LaMn}_4\text{Al}_8 \) on external pressure.

![FIG. 1. The \( \text{ThMn}_{12} \) structure into which the \( \text{RT}_4\text{Al}_8 \) compounds crystallize: the \( R \) atoms occupy 2(a) positions; the \( T \) atoms, 8(f) positions; and the Al atoms, two types of positions 8(i) and 8(j).](image-url)
pressure.\textsuperscript{14} It is very important to take this factor into account when comparing the properties of the RMn\textsubscript{4}Al\textsubscript{8} system and, perhaps, of the entire family of RT\textsubscript{4}Al\textsubscript{8} compounds.

There is essentially no information on the magnetism of the RCr\textsubscript{4}Al\textsubscript{8} compounds, except for some data on $\chi(T)$ for LuCr\textsubscript{4}Al\textsubscript{8} over a narrow temperature range.\textsuperscript{4} The nature of the magnetic properties of the RT\textsubscript{4}Al\textsubscript{8} family has been little studied up to now. In particular, there is also a lack of detailed theoretical calculations of the electronic structure of these compounds, except for Refs. 9 and 16, which deal with the magnetically ordered state of the compounds YFe\textsubscript{4}Al\textsubscript{8} and LuFe\textsubscript{4}Al\textsubscript{8}.

In this paper we study the features of the electronic spectrum and magnetic properties of the RT\textsubscript{4}Al\textsubscript{8} compounds with nonmagnetic elements \textit{R} = Sc, Y, La, and Lu and their evolution over the series of 3d-metals (T = Cr, Mn, and Fe), as well as their dependences on interatomic distance. The dependences of the magnetic susceptibility on temperature and hydrostatic pressure are studied experimentally for several representative compounds in this series. Systematic calculations of the electron structure and paramagnetic susceptibility of this family, including their dependence on the unit cell volume, are carried out in the electron density functional approximation.

2. Experimental details and results

The temperature dependences of the magnetic susceptibilities of polycrystalline samples of YFe\textsubscript{4}Al\textsubscript{8} and YMn\textsubscript{4}Al\textsubscript{8} were measured at temperatures of 4–300 K with a SQUID magnetometer. The $\chi(T)$ curves measured for YFe\textsubscript{4}Al\textsubscript{8} and published for ScFe\textsubscript{4}Al\textsubscript{8}\textsuperscript{2} and LuFe\textsubscript{4}Al\textsubscript{8}\textsuperscript{2} shown in Fig. 2 are similar in shape and have maxima at temperatures on the order of 100 K that can be identified as the Neel temperature $T_N$. The position of the maximum depends on the magnetic field strength and, for convenient comparison, these data correspond to roughly the same field, about 20 kOe. The similarity of the $\chi(T)$ curves for the RFe\textsubscript{4}Al\textsubscript{8} compounds (Fig. 2) and their weak dependence on the element \textit{R} imply a dominant role for the iron subsystem in the magnetism of this family. Note that in the paramagnetic state ($T > T_N$) the magnetic susceptibility of these compounds obeys the Curie-Weiss law only in a rough approximation and falls off more rapidly with increasing temperature.

As opposed to the family RFe\textsubscript{4}Al\textsubscript{8}, the RMn\textsubscript{4}Al\textsubscript{8} compounds, which have no magnetic ordering down to the lowest temperatures, have roughly an order of magnitude less magnetic moments than polycrystalline samples of YFe\textsubscript{4}Al\textsubscript{8} and YMn\textsubscript{4}Al\textsubscript{8} measured in a field of 0.2 kOe. ScMn\textsubscript{4}Al\textsubscript{8} and LuMn\textsubscript{4}Al\textsubscript{8} have similar $\chi(T)$ curves.\textsuperscript{15} Judging from the available data, for all these compounds at low temperatures there is a substantial increase in their susceptibility that is taken to be a small amount of free manganese ions in the samples.\textsuperscript{14,15} It is assumed that the corresponding contribution to the susceptibility has the form $C/T$, where the impurity Curie constant $C$ can be determined by representing the low-temperature susceptibility data as a function of the reciprocal temperature. In particular, we estimate that $C \approx 0.06$ K cm$^3$/mol for our sample of YMn\textsubscript{4}Al\textsubscript{8}, which implies that the amount of impurity manganese ions in the sample does not exceed 0.5%, assuming that their magnetic moment is $\sim 5.9\mu_B$. Subtracting this impurity contribution from the measured values of the susceptibility, we find the true temperature dependence $\chi(T)$ for the YMn\textsubscript{4}Al\textsubscript{8} sample shown as the dashed curve in Fig. 3(a), which is close to the data of Ref. 18.

As for the family RCr\textsubscript{4}Al\textsubscript{8} with nonmagnetic \textit{R} elements, there is almost no information on its magnetic properties and data have been published only for LuCr\textsubscript{4}Al\textsubscript{8}\textsuperscript{4} over a small temperature range (Fig. 3(b)). Our studies of this system were limited to the polycrystalline sample of CeCr\textsubscript{4}Al\textsubscript{8} available to us. Its magnetic susceptibility measured with a Faraday magnetometer in a field of 2 kOe is plotted as a function of temperature in Fig. 3(b). This curve is similar to the analogous data for LuCr\textsubscript{4}Al\textsubscript{8} in general, as well as in terms of the magnitude of the effect, which assumes that the contribution of the cerium ions to the magnetism of CeCr\textsubscript{4}Al\textsubscript{8} is small. It will be argued below that in this compound the cerium ion is actually nonmagnetic, since it is in the Ce$^{+3}$ valence state.

One of the main tasks of this paper was to study the effect of hydrostatic pressure in the magnetic susceptibility of these compounds. The susceptibility of samples of YFe\textsubscript{4}Al\textsubscript{8}, YMn\textsubscript{4}Al\textsubscript{8}, and CeCr\textsubscript{4}Al\textsubscript{8} under pressure was studied using a pendulum magnetometer with its mechanical part situated directly in the high-pressure chamber.\textsuperscript{19} Gaseous helium was used as the pressure transfer medium. Measurements were made under pressures \textit{P} of up to 2 kbar at temperatures of 78, 150, and 300 K in a magnetic field of 15–17 kOe. The relative error in the measurements did not exceed 0.1%. Figure 4
shows plots of the experimental $\chi(P)$ normalized to the magnetic susceptibility at zero pressure. It can be seen that, to within the measurement error, the effect is a linear function of $P$ for the pressure range used here. The corresponding values of the derivatives of the susceptibility with respect to pressure, $d\ln\chi/dP = \langle \Delta\chi/\chi \rangle/\Delta P$, are listed in Table 1 together with the initial values of the susceptibility.

For YMn$_4$Al$_8$ the table also lists the intrinsic susceptibilities $\chi_0 = \chi - C/T$ corrected for the impurity contributions and their baric derivatives, defined as $d\ln\chi_0/dP = (\Delta\chi/\chi_0)d\ln\chi/dP$ under the assumption that the impurity contribution is independent of pressure.

It can be seen from Fig. 4 and Table 1 that in YFe$_4$Al$_8$ and CeCr$_4$Al$_8$ the pressure effect is moderately large and is characteristic, in terms of sign and magnitude, of typical exchange-enhanced band paramagnets. As for YMn$_4$Al$_8$, the increase in the pressure effect observed in it is quite unexpected and requires detailed analysis.

### 3. Calculations of the electronic structure and magnetic susceptibility of the RT$_4$Al$_8$ compounds

The RT$_4$Al$_8$ family has a volume-centered tetragonal crystal structure that belongs to the symmetry space group $I4/mmm$. The electronic structure was calculated using a modified relativistic LMTO method with the full potential (FP-LMTO, version RSP) and the linearized associated plane wave method with the full potential (FP-LAPW, version E1k). The exchange-correlation potential was included both in terms of a local density approximation (LDA) and in the generalized gradient approximation (GGA) of the density functional theory (DFT). The electronic structures of the RT$_4$Al$_8$ compounds were calculated using expansions in spherical harmonics of the basis wave functions inside “muffin-tin” spheres with conservation of the principal $n$ and orbital $l$ quantum numbers corresponding to the outer electron shells of the atoms. During the self-consistent calculations of the crystalline potential the states of the ion core were calculated separately in each iteration, i.e., the “frozen core” approximation was not used. This greatly increased the accuracy and reliability of the calculations. No limitations were imposed on the charge density or potential in the full potential FP-LMTO and FP-LAPW methods used here; this

<table>
<thead>
<tr>
<th>Quantity</th>
<th>$T$ (K)</th>
<th>YFe$_4$Al$_8$</th>
<th>YMn$_4$Al$_8$</th>
<th>CeCr$_4$Al$_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_0$</td>
<td>78</td>
<td>3.74</td>
<td>4.99</td>
<td>5.90</td>
</tr>
<tr>
<td>$-d\ln\chi_0/dP$</td>
<td>78</td>
<td>4.8 $\pm$ 0.3</td>
<td>12.1 $\pm$ 1</td>
<td>8.6 $\pm$ 1</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>7.8 $\pm$ 0.4</td>
<td>25.6 $\pm$ 1</td>
<td>6.2 $\pm$ 1</td>
</tr>
<tr>
<td>$\chi_0$</td>
<td>78</td>
<td>3.74</td>
<td>4.99</td>
<td>5.90</td>
</tr>
<tr>
<td>$-d\ln\chi_0/dP$</td>
<td>78</td>
<td>4.8 $\pm$ 0.3</td>
<td>12.1 $\pm$ 1</td>
<td>8.6 $\pm$ 1</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>7.8 $\pm$ 0.4</td>
<td>25.6 $\pm$ 1</td>
<td>6.2 $\pm$ 1</td>
</tr>
</tbody>
</table>

FIG. 4. Experimental plots of the magnetic susceptibility of several RT$_4$Al$_8$ compounds, normalized to the susceptibility at $P = 0$, as a function of pressure. The points (C) and (●) correspond to temperatures of 300 and 78 K.
was especially important for the anisotropic layered structures of the compounds studied here.

Figures 5–7 show the calculated densities of electronic states $N(E)$ in the paramagnetic (PM) phase, which give an idea of the evolution of the electronic structure of the RT$_4$Al$_8$ compounds in the sequence $T = \text{Cr} \rightarrow \text{Mn} \rightarrow \text{Fe}$. Calculated densities of states at the Fermi level and their derivatives with respect to volume are listed in Table 2. Note that the dominant contribution to $N(E_F)$ is from the $d$-states of the 3$d$-metal.

Figure 5 shows that for the PM phase of RFe$_4$Al$_8$, the Fermi level lies in a steep segment of the $N(E)$ curve, where the density of states increases rapidly with energy immediately adjacent ($\sim 0.01$ eV) to a sharp peak in the density of electronic states. The densities of states of the isoelectronic compounds RFe$_4$Al$_8$ are extremely similar and differ only in negligible details.

In order to analyze the magnetoelastic properties of the RT$_4$Al$_8$ compounds we have calculated the volume dependence of the total electronic energy $E_{\text{tot}}(V)$ in the generalized gradient approximation (GGA), which provides the most adequate description of the structural and elastic properties of metallic systems. The hydrostatic compression moduli $B$ in these compounds were calculated by parametrizing $E_{\text{tot}}(V)$ using the Murnahan equation

$$E_{\text{tot}}(V) = E_0 + \frac{B V_0}{B'} \left( \frac{(V/V_0)^{B'/B} - 1}{B'/B - 1} + \frac{V}{V_0} - \frac{B'}{B - 1} \right),$$

where $B = B(V_0)$. The Murnahan equation is based on the assumption that the derivative of $B$ with respect to pressure, $B'$, is constant. The calculated values of the elastic moduli $B$ of the RT$_4$Al$_8$ compounds are listed in Table 2 and are close to 1.4 Mbar. It should be noted that there are no published data on the elastic moduli of the RT$_4$Al$_8$ systems.

We have also calculated the spin-polarized electronic structure of a series of RMn$_4$Al$_8$ and RCr$_4$Al$_8$ compounds in an external magnetic field $\mathbf{H}$ by the FP-LMTO method. Here the effect of the external magnetic field on the electronic
TABLE 2. Calculated values of the density of electronic states at the Fermi level \( N(E_F) \) (states/eV-form unit), its volume derivative \( d N(E_F)/d \ln V \), and hydrostatic compression moduli \( B \) (Mbar) for the series of compounds \( RT_4Al_8 \).

<table>
<thead>
<tr>
<th>Compound</th>
<th>( N(E_F) )</th>
<th>( d N(E_F)/d \ln V )</th>
<th>( B )</th>
</tr>
</thead>
<tbody>
<tr>
<td>YFe(_4)Al(_8)</td>
<td>27.2</td>
<td>2.24</td>
<td>1.41</td>
</tr>
<tr>
<td>LuFe(_4)Al(_8)</td>
<td>27.1</td>
<td>2.30</td>
<td>1.45</td>
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<td>ScMn(_4)Al(_8)</td>
<td>7.6</td>
<td>1.50</td>
<td>1.49</td>
</tr>
<tr>
<td>YMn(_4)Al(_8)</td>
<td>7.8</td>
<td>1.48</td>
<td>1.45</td>
</tr>
<tr>
<td>LaMn(_4)Al(_8)</td>
<td>8.7</td>
<td>1.38</td>
<td>1.40</td>
</tr>
<tr>
<td>LuMn(_4)Al(_8)</td>
<td>7.8</td>
<td>1.56</td>
<td>1.46</td>
</tr>
<tr>
<td>YCr(_4)Al(_8)</td>
<td>13.8</td>
<td>1.40</td>
<td>1.36</td>
</tr>
<tr>
<td>LuCr(_4)Al(_8)</td>
<td>13.5</td>
<td>1.57</td>
<td>1.37</td>
</tr>
<tr>
<td>LaCr(_4)Al(_8)</td>
<td>16.6</td>
<td>1.50</td>
<td>1.30</td>
</tr>
<tr>
<td>CeCr(_4)Al(_8)</td>
<td>16.2</td>
<td>0.95</td>
<td>1.39</td>
</tr>
</tbody>
</table>

The electronic density of states at the Fermi level \( N(E_F) \) for the \( RT_4Al_8 \) compounds (see Table 2) can be compared with the available experimental data on the electronic specific heat \( \gamma \) shown in Table 5. The difference between \( \gamma_{\text{calc}} \) and \( \gamma_{\text{exp}} \) is usually explained in terms of a renormalization of the effective masses of the single-electron spectrum by electron-phonon interactions, with

\[
\gamma_{\text{exp}} = (1 + \lambda)\gamma_{\text{calc}},
\]

which makes it possible to determine the corresponding renormalization parameter \( \lambda \) (see Table 5).

4. Discussion of results

We note first that the data of Fig. 5 on the electronic density of states \( N(E_F) \) for the \( RFe_4Al_8 \) compounds (see Table 2) can be compared with the available experimental data on the electronic specific heat \( \gamma \) shown in Table 5. The difference between \( \gamma_{\text{calc}} \) and \( \gamma_{\text{exp}} \) is usually explained in terms of a renormalization of the effective masses of the single-electron spectrum by electron-phonon interactions, with

\[
\gamma_{\text{exp}} = (1 + \lambda)\gamma_{\text{calc}},
\]

which makes it possible to determine the corresponding renormalization parameter \( \lambda \) (see Table 5).
The values of $\gamma_{\text{calc}}$ for YFe$_4$Al$_8$ and LuFe$_4$Al$_8$ in Table 5 correspond to the electron densities of states of the compounds at the Fermi level for the antiferromagnetic phase calculated in Ref. 16. The corresponding experimental values of $\gamma_{\text{exp}}$ in Table 5 were also obtained for the AFM state of the YFe$_4$Al$_8$ and LuFe$_4$Al$_8$ at low temperatures. According to Eq. (3), the renormalization parameter for the effective masses of the one-electron spectrum for these compounds is $\lambda = 1$, which agrees qualitatively with the observation of superconductivity in LuFe$_4$Al$_8$ and YFe$_4$Al$_8$.

However, the contribution to $\lambda$ of the spin-fluctuation term $\lambda_{\text{sf}}$, $\lambda = \lambda_{\text{el-ph}} + \lambda_{\text{sf}}$, should also be taken into account, as it can be quite large for systems with high $N(E_F)$. The estimate of the electron-phonon renormalization $\lambda_{\text{el-ph}}$, therefore, remains unsettled, as does the origin of superconductivity in the RFe$_4$Al$_8$ compounds. We note also that the anomalously high $\gamma_{\text{exp}}$ observed in some compounds, such as LaMn$_4$Al$_8$, can be explained by a spin-fluctuation mechanism, as well as by the possible presence of magnetic impurities and structural defects in the samples studied here.

The self-consistent FP-LMTO-LSDA calculations of the spin polarized electron structure in an external magnetic field yielded values for the magnetic susceptibility in the RMn$_4$Al$_8$ and RCr$_4$Al$_8$ systems that agree well with experimental data (see Tables 3 and 4). This method of calculating $\gamma$ ensures that the nonuniform distribution of the spin density in the unit cell and volume-correlation interaction effects are correctly taken into account, so that the agreement between the calculated and experimental susceptibilities is considerably better. According to these calculations, the dominant contribution to the magnetic susceptibility of the RT$_4$Al$_8$ compounds is from exchange-enhanced spin paramagnetism, $\gamma_{\text{spin}}$. An approximate estimate of the parameters characterizing this contribution can be obtained using the Stoner model

$$\gamma_{\text{spin}} = \frac{\gamma_P}{1 - \alpha \gamma_P} \equiv S \gamma_P,$$

where $\gamma_P = \mu_B^2 N(E_F)$ is the Pauli susceptibility, $\alpha = J / 2 \mu_B^2$ is the molecular field constant, $J$ is the exchange integral, and $S$ is the Stoner factor. Typical values of the parameters in Eq. (4) estimated for some of the RT$_4$Al$_8$ compounds using the calculated $\gamma_P$ and $\gamma_{\text{spin}}$ are given in Table 6.

A comparison of the calculated values of $\gamma_{\text{spin}}$ (Table 6) with theoretical values of the total susceptibility $\gamma = \gamma_{\text{spin}} + \gamma_{\text{orb}}$ (Tables 3 and 4) shows that in the systems RMn$_4$Al$_8$ and RCr$_4$Al$_8$ studied here, the van Vleck orbital contribution $\gamma_{\text{orb}}$ is as high as 10% of the total susceptibility and must be taken into account in a quantitative analysis of the experimental data. We note that the calculated contribution of $\gamma_{\text{orb}}$ for CeCr$_4$Al$_8$ is about 20% of the total susceptibility and is determined mainly by the electronic states of the cerium atom, where the 4f-electron is assumed to be delocalized because of strong hybridization with the valence d-states and to be participating in chemical bonding (see Fig. 7).

This assumption is supported by the good agreement between the calculated and experimental values of the lattice parameters and magnetic susceptibility of CeCr$_4$Al$_8$.

The experimental pressure dependences of $\gamma$ for the RMn$_4$Al$_8$ and RCr$_4$Al$_8$ systems scaled to volume derivatives with a bulk compression modulus $B \approx 1.4$ Mbar are listed in Tables 3 and 4 together with the theoretical values of $d\ln \gamma / d\ln V$ corresponding to the dependences in Figs. 8 and 9. The tables show that the calculated $d\ln \gamma / d\ln V$ are in good agreement with experimental data from the experiments on magnetic susceptibility under pressure. In addition, for the most studied system RMn$_4$Al$_8$, the calculated data correlate with the dependence of the magnetic susceptibility in the sequence $R =$ Sc, Y, La, and Lu on the unit cell volume under normal conditions (Fig. 10), which, in a log-log plot, is close to linear and determined by the derivative $d\ln \gamma / d\ln V \approx 2$. This estimate of the effect of chemical pressure is comparable to the calculated and experimental values of the parameter $\lambda$ of RT$_4$Al$_8$ compounds.

### Table 5. Calculated and experimental values of the electronic thermal conductivity $\gamma$ (in units of mJ/mol K$^2$) and of the parameter $\lambda = \gamma_{\text{exp}} / \gamma_{\text{calc}} - 1$ for the series of RT$_4$Al$_8$ compounds.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>$\gamma_{\text{calc}}$</th>
<th>$\gamma_{\text{exp}}$</th>
<th>$\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>YFe$_4$Al$_8$</td>
<td>34 (Ref. 16)</td>
<td>60 (Ref. 26)</td>
<td>0.8</td>
</tr>
<tr>
<td>LuFe$_4$Al$_8$</td>
<td>33 (Ref. 16)</td>
<td>75 (Ref. 10)</td>
<td>1.3</td>
</tr>
<tr>
<td>YMn$_4$Al$_8$</td>
<td>18.4</td>
<td>95.27 (Ref. 28)</td>
<td>4.2; 3.5</td>
</tr>
<tr>
<td>LaMn$_4$Al$_8$</td>
<td>20.5</td>
<td>265 (Ref. 28)</td>
<td>12</td>
</tr>
<tr>
<td>YCr$_4$Al$_8$</td>
<td>32.5</td>
<td>220 (Ref. 11)</td>
<td>5.8</td>
</tr>
<tr>
<td>LaCr$_4$Al$_8$</td>
<td>39.1</td>
<td>58 (Ref. 26)</td>
<td>0.5</td>
</tr>
<tr>
<td>CeCr$_4$Al$_8$</td>
<td>38.2</td>
<td>62, 26 $^{26}$ 180 (Ref. 29)</td>
<td>0.6; 4.7</td>
</tr>
</tbody>
</table>

### Table 6. Calculated values of the parameters $\gamma_P$ and $\gamma_{\text{spin}}$ (10$^{-3}$ cm$^3$/mol), molecular field constant $x$ (10$^{-3}$ cm$^3$/mol), and Stoner factor $S$ of RT$_4$Al$_8$ compounds (for YFe$_4$Al$_8$ $x$ is estimated using the Stoner criterion for magnetic ordering in Eq. (4), $\sigma_P \geq 1$).

<table>
<thead>
<tr>
<th>Quantity</th>
<th>$\gamma_P$</th>
<th>$\gamma_{\text{spin}}$</th>
<th>$\alpha$</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>YFe$_4$Al$_8$</td>
<td>0.880</td>
<td>...</td>
<td>≥1.1</td>
<td>...</td>
</tr>
<tr>
<td>YMn$_4$Al$_8$</td>
<td>0.252</td>
<td>4.04</td>
<td>3.72</td>
<td>16</td>
</tr>
<tr>
<td>LaMn$_4$Al$_8$</td>
<td>0.282</td>
<td>13.3</td>
<td>3.47</td>
<td>47</td>
</tr>
<tr>
<td>YCr$_4$Al$_8$</td>
<td>0.446</td>
<td>6.16</td>
<td>2.08</td>
<td>14</td>
</tr>
<tr>
<td>LaCr$_4$Al$_8$</td>
<td>0.537</td>
<td>4.30</td>
<td>1.63</td>
<td>8</td>
</tr>
<tr>
<td>CeCr$_4$Al$_8$</td>
<td>0.524</td>
<td>3.87</td>
<td>1.65</td>
<td>7.4</td>
</tr>
</tbody>
</table>
values of the volume derivative $d \ln \chi / d \ln V$ in this sequence (see Table 3) and indicates that the interatomic distance plays a significant role in the magnetism of the RMn$_4$Al$_8$ compounds.

In terms of the Stoner model (4), in systems with a predominance of spin paramagnetism ($\chi \approx \chi_{\text{spin}}$) in their susceptibility, the magnetovolume effect is determined by the expression

$$\frac{d \ln \chi}{d \ln V} \approx \frac{d \ln \chi_p}{d \ln V} + \chi \left( \frac{d \ln \chi}{d \ln V} + \frac{d \ln \chi_p}{d \ln V} \right),$$

(5)

which is convenient for describing the temperature dependence of the magnetovolume effect determined mainly by the $\chi(T)$ dependence. Substituting the experimental values of $d \ln \chi_p / d \ln V$ at $T = 300$ K for YMn$_4$Al$_8$ ($\sim$37 according to our data) and for LaMn$_4$Al$_8$ ($\sim$55 (Ref. 14)), together with the calculated value $d \ln \chi_p / d \ln V \equiv d \ln N(E_F) / d \ln V \approx 1.5$, yields a value for the volume derivative of the molecular field constant $\chi$ in the RMn$_4$Al$_8$ compounds within a range of

$$\frac{d \ln \chi}{d \ln V} \approx -0.3.$$  

(6)

A similar value of the derivative $d \ln \chi / d \ln V \sim 0.4$ follows from Eq. (5) for CeCr$_4$Al$_8$ when the corresponding experimental data for $T = 78$ K are used.

We note that for CeCr$_4$Al$_8$ the calculated value of the volume derivative of $\chi$ was roughly a factor of 1.5 smaller than the corresponding derivatives for the other RCr$_4$Al$_8$ compounds (Table 3). This appears to be related to the tetravalent state of the cerium ion in CeCr$_4$Al$_8$ and to the difference in the filling of the conduction band relative to the other RCr$_4$Al$_8$ systems, where the Y, La, and Lu ions are trivalent. The available data on a relatively weak volume dependence of $\chi$ in the RMn$_4$Al$_8$ and RCr$_4$Al$_8$ systems are in sharp contrast with the typical values $d \ln \chi / d \ln V \equiv d \ln J / d \ln V = -(0.7 - 1.5)$ for strong band paramagnetic materials$^{30,31}$ and with the value

$$\frac{d \ln \chi}{d \ln V} \approx -2$$  

(7)

for YFe$_4$Al$_8$ given by Eq. (5) with the corresponding experimental values of $d \ln \chi / d \ln V$ for $T = 300$ K and the calculated values $\chi_p / d \ln V = 2.24$ and $\chi \approx 1.1 \times 10^4$ mol/cm$^3$.

One possible reason for the highly different and hard-to-explain behavior of the exchange interaction in these compounds of a single type may be the limited applicability of the Stoner model that we have used in systems with a highly nonuniform electron density. This nonuniformity is typical, in particular, for quasi-one-dimensional chains of equidistant atoms of a 3$d$-meta in the structure of RT$_4$Al$_8$ compounds, when the distance between these atoms along the crystal c axis is considerably smaller than the distances between neighbors in the perpendicular directions. It should be noted, however, that the Stoner model provides a quite reasonable description of the experimentally observed pressure effect with varying temperature, an effect which is determined by $\chi(T)$ according to Eq. (5).

5. Conclusion

In this paper we have carried out the first systematic calculations of the electronic structure and magnetic properties of the family of compounds RT$_4$Al$_8$, where R denotes a non-magnetic element Sc, Y, La, or Lu and T = Fe, Mn, or Cr. DFT calculations have been made of the electronic spectrum and magnetic susceptibility of these compounds in the paramagnetic phase and of their behavior when the lattice parameters are varied. The results indicate that exchanged-enhanced spin paramagnetism predominates in the magnetic susceptibility of the entire RT$_4$Al$_8$ family and that the magnetovolume effect $d \ln \chi / d \ln V$ is anomalously large in the RMn$_4$Al$_8$ and RCr$_4$Al$_8$ systems. The calculated values are in reasonable agreement with experimental data on the magnetic susceptibility and its pressure dependence. This confirms the adequacy of the DFT method for describing the magnetism of complicated intermetallic compounds of the 3$d$-metals.

Refinement of the magnetic characteristics of the RT$_4$Al$_8$ family and further clarification of the large magnetovolume effect in the compounds with manganese and chromium, presumably caused by the unusual volume dependence of the parameter $J$, will require further detailed experimental studies of high-quality, single-crystal samples, along with the development of theoretical approaches for describing the magnetic properties at finite temperatures.

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22See http://fplmto-rspt.org/

23See http://elk.sourceforge.net/


Translated by D. H. McNeill