

Electronic structure and magnetic properties of RT_4AI_8 (R = Sc, Y, La, Lu; T = Fe, Mn, Cr) compounds. Hydrostatic pressure effects

I. P. Zhuravleva, G. E. Grechnev, A. S. Panfilov,^{a)} A. A. Lyogenkaya, and O. V. Kotlyar

B. I. Verkin Institute of Low-temperature Physics and Engineering, National Academy of Sciences of Ukraine, pr. Nauki 47, Kharkov 61103, Ukraine

A. V. Fedorchenko

B. I. Verkin Institute of Low-temperature Physics and Engineering, National Academy of Sciences of Ukraine, pr. Nauki 47, Kharkov 61103, Ukraine and Institute of Physics, Faculty of Science, P. J. Šafárik University in Košice, Košice 04154, Slovakia

A. Feher

Institute of Physics, Faculty of Science, P. J. Šafárik University in Košice, Košice 04154, Slovakia (Submitted February 25, 2016) Fiz. Nizk. Temp. **42**, 586–595 (June 2016)

We present results of theoretical and experimental studies of the electronic structure and magnetic properties of RFe_4Al_8 , RMn_4Al_8 , and RCr_4Al_8 compounds with nonmagnetic elements R = Sc, Y, La, and Lu. The electron spectrum and field induced magnetic moment, as well as their dependences on the unit cell volume, are calculated for the paramagnetic phase of the RT_4Al_8 systems. The calculations are supplemented by measurements of the magnetic susceptibility of representative RT_4Al_8 compounds as a function of temperature and hydrostatic pressure. *Published by AIP Publishing*. [http://dx.doi.org/10.1063/1.4954784]

1. Introduction

 RT_4Al_8 compounds (where R is a rare earth element and T = Fe, Mn, Cr) crystallize into a tetragonal crystal structure of the type $ThMn_{12}$ (Fig. 1) and have a great variety of magnetic properties.^{1–5} This variety shows up most clearly in the compounds with T = 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 RT_4Al_8 compounds with a nonmagnetic element R from the lanthanum group (R-Sc, Y, La, Lu) are determined predominantly by the 3*d*-sublattice of the metal. The weak dependence of the magnetic properties on the element R shows up most clearly in the RFe₄Al₈ compounds; this is explained by the dominant contribution of the 3*d*-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 RFe₄Al₈ family is the detection of traces of a superconducting phase in the compounds ScFe₄Al₈($T_c = 6K$), YFe₄Al₈($T_c = 6K$), and LuFe₄Al₈($T_c \sim 24K$) in studies of their surface resistivity and specific heat,^{10,11} well as in YFe₄Al₈ 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 RFe₄Al₈ 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 RMe₄Al₈ 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 RMn₄Al₈ compounds is the significant influence of chemical pressure effects on their magnetism, as confirmed by an anomalously high dependence of the magnetic susceptibility LaMn₄Al₈ on external



FIG. 1. The Th Mn_{12} structure into which the RT_4Al_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).

pressure.¹⁴ It is very important to take this factor into account when comparing the properties of the RMn₄Al₈ system and, perhaps, of the entire family of RT₄Al₈ compounds.

There is essentially no information on the magnetism of the RCr₄Al₈ compounds, except for some data on $\chi(T)$ for LuCr₄Al₈ over a narrow temperature range.⁴ The nature of the magnetic properties of the RT₄Al₈ 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 YFe₄Al₈ and LuFe₄Al₈.

In this paper we study the features of the electronic spectrum and magnetic properties of the RT_4Al_8 compounds with nonmagnetic elements R = Sc, Y, La, and Lu and their evolution over the series of 3*d*-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 YFe₄Al₈ and YMn₄Al₈ were measured at temperatures of 4-300 K with a SQUID magnetometer. The $\chi(T)$ curves measured for YFe₄Al₈ and published for $ScFe_4Al_8^{17}$ and $LuFe_4Al_8^2$ 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 RFe₄Al₈ compounds (Fig. 2) and their weak dependence on the element 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 RFe₄Al₈, the RMn₄Al₈ compounds, which have no magnetic ordering down to the lowest temperatures, have roughly an order of magnitude less paramagnetism with an essentially nonmonotonic temperature dependence of the susceptibility. Figure 3(a) shows experimental $\chi(T)$ curves for LaMn₄Al₈ and YMn₄Al₈ measured in a magnetic field of 10 KOe,14 along with our data for YMn₄Al₈ measured in a field of 0.2 kOe. ScMn₄Al₈ and LuMn₄Al₈ have similar $\chi(T)$ curves.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.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 $C \approx 0.06 \,\mathrm{K} \,\mathrm{cm}^3/\mathrm{mol}$ for our sample



FIG. 2. Magnetic susceptibility as a function of temperature for YFe_4Al_8 (this paper), $ScFe_4Al_8$, 17 and $LuFe_4Al_8$.²

of YMn₄Al₈, 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 YMn₄Al₈ sample shown as the dashed curve in Fig. 3(a), which is close to the data of Ref. 18.

As for the family RCr_4Al_8 with nonmagnetic R elements, there is almost no information on its magnetic properties and data have been published only for $LuCr_4Al_8^4$ over a small temperature range (Fig. 3(b)). Our studies of this system were limited to the polycrystalline sample of $CeCr_4Al_8$ 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 $LuCr_4Al_8$ 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 $CeCr_4Al_8$ is small. It will be argued below that in this compound the cerium ion is actually nonmagnetic, since it is in the Ce^{4+} 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 YFe₄Al₈, YMn₄Al₈, and CeCr₄Al₈ under pressure was studied using a pendulum magnetometer with its mechanical part situated directly in the high-pressure chamber.¹⁹ Gaseous helium was used as the pressure transfer medium. Measurements were made under pressures *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



FIG. 3. Temperature dependences of the magnetic susceptibility for $LaMn_4Al_8(\bigcirc) K$ and $YMn_4Al_8(\bigcirc)^{14}$ and data from the present work for YMn_4Al_8 (\bullet); the dashed curve is corrected data with the low-temperature impurity contribution subtracted (see text for details) (a); (\bigcirc) data for $LaCr_4Al_8^4$ and (\bullet) data for $CeCr_4Al_8$ from the present work.

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, $d\ln\chi/dP \equiv (\Delta\chi/\chi)/\Delta P$, are listed in Table 1 together with the initial values of the susceptibility.

For YMn₄Al₈ the table also lists the intrinsic susceptibilities $\chi_0 = \chi - C/T$ corrected for the impurity contributions and their baric derivatives, defined as $d \ln \chi_0 / dP = (\chi/\chi_0) d \ln \chi / dP$ under the assumption that the impurity contribution is independent of pressure.

It can be seen from Fig. 4 and Table 1 that in YFe_4Al_8 and $CeCr_4Al_8$ the pressure effect is moderately large and is characteristic, in terms of sign and magnitude, of typical exchange-enhanced band paramagnets.²⁰ As for YMn_4Al_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_4Al_8 compounds

The RT_4Al_8 family has a volume-centered tetragonal crystal structure that belongs to the symmetry space group *I4/mmm*.⁵ The electronic structure was calculated using a modified relativistic LMTO method with the full potential (FP-LMTO, version RSPt^{20–22}) and the linearized associated plane wave method with the full potential (FP-LAPW, version E1k²³). The exchange-correlation potential was included



FIG. 4. Experimental plots of the magnetic susceptibility of several RT_4AI_8 compounds, normalized to the susceptibility at P = 0, as a function of pressure. The points (\bigcirc) and (\bigcirc) correspond to temperatures of 300 and 78 K.

both in terms of a local density approximation $(LDA)^{24}$ and in the generalized gradient approximation $(GGA)^{25}$ of the density functional theory (DFT). The electronic structures of the RT₄Al₈ 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 1. Experimental values of the magnetic susceptibility $\chi (10^{-3} \text{ cm}^3/\text{mol})$ and its baric derivative $d\ln\chi/dP$ (Mbar⁻¹) in RT₄Al₈ compounds, together with the corresponding values of these quantities for YMn₄Al₈ corrected for the impurity contribution, χ_0 and $d\ln\chi_0/dP$ (see text for details).

Quantity	$T(\mathbf{K})$	YFe ₄ Al ₈	YMn_4Al_8	CeCr ₄ Al ₈
χ	78	90.8	4.49	3.63
	150	67.6		
	300	28.9	5.50	2.69
$-d \ln \chi/dP$	78	4.8 ± 0.3	12.1 ± 1	8.6 ± 1
	150	7.8 ± 0.4		
	300	5.1 ± 0.2	25.6 ± 1	6.2 ± 1
χο	78		3.74	
	300		5.30	
$-d \ln \chi_0/dP$	78		14.5 + 1	
	300		26.5 + 1	

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 RT₄Al₈ compounds in the sequence $T = Cr \rightarrow Mn \rightarrow Fe$. Calculated densities of states of the RT₄Al₈ compounds 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_4Al_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 (~0.01 eV) to a sharp peak in the density of electronic states. The densities of states of the isoelectronic compounds RFe_4Al_8 are extremely similar and differ only in negligible details.

In order to analyze the magnetoelastic properties of the RT_4Al_8 compounds we have calculated the volume dependence of the total electronic energy $E_{tot}(V)$ in the generalized gradient approximation (GGA),²⁵ which provides the most adequate description of the structural and elastic properties of metallic systems.²¹ The hydrostatic compression moduli *B* in these compounds were calculated by parametrizing $E_{tot}(V)$ using the Murnahan equation

$$E_{\text{tot}}(V) = E_0 + \frac{BV_0}{B'} \left(\frac{(V_0/V)^{B'-1}}{B'-1} + \frac{V}{V_0} - \frac{B'}{B'-1} \right), \quad (1)$$



FIG. 5. Electron densities of state of RFe_4Al_8 (R = Sc, Y, and Lu) compounds. The Fermi level at E = 0 is indicated by the vertical dashed line.



FIG. 6. Electron densities of state N(E) of YT_4Al_8 (T = Cr, Mn, and Fe) compounds.

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 RT₄Al₈ 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 RT₄Al₈ systems.

We have also calculated the spin-polarized electronic structure of a series of RMn_4Al_8 and RCr_4Al_8 compounds in an external magnetic field **H** by the FP-LMTO method.²⁰ Here the effect of the external magnetic field on the electronic



FIG. 7. Density of electronic states of the compound $CeCr_4Al_8$. The partial contribution of the 4*f*-state of cerium is indicated by the shaded region.

TABLE 2. Calculated values of the density of electronic states at the Fermi level $N(E_F)$ (states/eV·form.unit), its volume derivative $d\ln N(E_F)/d\ln V$, and hydrostatic compression modulus *B* (Mbar) for the series of compounds RT₄Al₈.

Compound	$N(E_F)$	$d\ln N (E_F)/d\ln V$	В
YFe ₄ Al ₈	27.2	2.24	1.41
LuFe ₄ Al ₈	27.1	2.30	1.45
ScMn ₄ Al ₈	7.6	1.50	1.49
YMn ₄ Al ₈	7.8	1.48	1.45
LaMn ₄ Al ₈	8.7	1.38	1.40
LuMn ₄ Al ₈	7.8	1.56	1.46
YCr ₄ Al ₈	13.8	1.40	1.36
LuCr ₄ Al ₈	13.5	1.57	1.37
LaCr ₄ Al ₈	16.6	1.50	1.30
CeCr ₄ Al ₈	16.2	0.95	1.39

structure of the paramagnetic phase was taken into account self consistently in terms of the local spin density approximation LSDA²⁴ by including the Zeeman operator

$$\mathcal{H}_Z = \mu_B \mathbf{H} \cdot (2\hat{\mathbf{s}} + \hat{\mathbf{I}}) \tag{2}$$

in the FP-LMTO Hamiltonian, where \hat{s} is the spin operator and \hat{I} is the orbital angular momentum operator. The calculated induced spin and orbital magnetic moments in the external field **H** made it possible to obtain the corresponding components, χ_{spin} and χ_{orb} , of the magnetic susceptibility by differentiating the induced magnetizations with respect to the field. Note that for the systems RMn₄Al₈ and RCr₄Al₈, the spin contributions to the susceptibility χ_{spin} are roughly an order of magnitude greater than the orbital contributions χ_{orb} .

Calculated magnetic susceptibilities of RMn₄Al₈ and RCr₄Al₈ compounds and their derivatives with respect to volume are listed in Tables 3 and 4, respectively. The calculated volume dependences of the magnetic susceptibilities of RMn₄Al₈ and RCr₄Al₈ compounds are shown in Figs. 8 and 9. It should be noted that for the RFe₄Al₈ compounds the spinpolarized calculations in an external field were unstable. Because of the large values of $N(E_F)$ and the closeness of these systems to a ferromagnetic state, it was not possible to obtain the paramagnetic response to the external field and the self-consistent calculations of the spin polarized electronic structure yielded a moment of about $1.3\mu_B$ per iron atom.

4. Discussion of results

We note first that the data of Fig. 5 on the electronic density of states N(E) in RFe₄Al₈ compounds and their evolution

TABLE 3. Calculated and experimental values of the magnetic susceptibility χ (10⁻³ cm³/mol) and its volume derivative $d\ln\chi/d\ln V$ at T = 78 K for RMn₄Al₈ compounds (we have corrected the experimental data with a pressure-independent impurity contribution assumed to be caused by free manganese ions).

Quantity	ScMnpAR	YMnpAR	LaMn ₄ Al ₈	LuMnpAR
Theory				
χ	2.1	4.35	13.8	3.1
$d \ln \chi/d \ln V$	13	26	33	18
Experiment				
$\chi (T \rightarrow 0K)$	~2.5 (Ref. 15)	4	~12 (Ref. 14)	~3.5 (Ref. 15)
$d \ln \chi / d \ln V$		20 ± 2	\sim 55 (Ref. 14)	

TABLE 4. Calculated and experimental values of the magnetic susceptibility χ (10⁻³ cm³/mol) and its volume derivative $d\ln\chi/d\ln V$ at T = 78 K for RCr₄Al₈ compounds.

Quantity	YCr ₄ Al ₈	LaCr ₄ Al ₈	LuCr ₄ Al ₈	CeCr ₄ Al ₈
Theory				
χ	6.5	4.5	3.8	4.9
$d \ln \chi/d \ln V$	20	~ 15	16.5	11
Experiment				
$\chi (T \rightarrow 0K)$			4.1 (Ref. 4)	~ 4.5
$d \ln \chi/d \ln V$				12

along the sequence T = Fe, Mn, and Cr for the example of YT_4Al_8 compounds (Fig. 6) reflect the magnetic properties of this system as a whole. Thus, the magnetic ordering and strong reduction in the susceptibility of the paramagnetic phase with increasing temperature observed in the RFe₄Al₈ compounds are caused by the sharp peak in N(E) at a high density of states $N(E_F)$ near the Fermi level. In the RMn₄Al₈ compounds the Fermi level lies at a minimum of N(E); this correlates with the observed increase in the susceptibility at moderate temperatures, while the rather flat maximum of N(E) in the RCr₄Al₈ compounds determines the comparatively small reduction in their susceptibility with increasing temperature. Here the significantly lower values of $N(E_F)$ in the compounds with manganese and chromium explain the absence of magnetic ordering in these compounds.

The electronic density of states at the Fermi level $N(E_F)$ calculated for the RT₄Al₈ compounds (see Table 2) can be compared with the available experimental data on the electronic specific heat γ_{exp} shown in Table 5. The difference between γ_{calc} and γ_{exp} is usually explained in terms of a renormalization of the effective masses of the single-electron spectrum by electron-phonon interactions, with

$$\gamma_{\exp} = (1+\lambda)\gamma_{\text{calc}},\tag{3}$$

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



FIG. 8. Calculated dependences of the magnetic susceptibility of RMn₄Al₈ compounds on the unit cell volume. The arrows indicate the experimental values of the volume under normal conditions.



FIG. 9. Calculated dependences of the magnetic susceptibility of RCr_4Al_8 compounds on the unit cell volume. The arrows indicate the experimental values of the volume under normal conditions.

The values of γ_{calc} for YFe₄Al₈ and LuFe₄Al₈ 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 γ_{exp} in Table 5 were also obtained for the AFM state of the YFe₄Al₈ and LuFe₄Al₈ 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_4Al_8 and $\mathrm{YFe_4Al_8}^{10,11}$ However, the contribution to λ of the spin-fluctuation term λ_{sf} , $\lambda = \lambda_{el-ph} + \lambda_{sf}$, should also be taken into account, as it can be quite large for systems with high $N(E_F)$.²⁰ The estimate of the electron-phonon renormalization λ_{el-ph} , therefore, remains unsettled, as does the origin of superconductivity in the RFe₄Al₈ compounds. We note also that the anomalously high γ_{exp} observed in some compounds, such as LaMn₄Al₈, 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_4Al_8 and RCr_4Al_8 systems that agree well with experimental data (see Tables 3 and 4). This method of calculating

TABLE 5. Calculated and experimental values of the electronic thermal conductivity γ (in units of mJ/mol-K²) and of the parameter $\lambda = \gamma_{exp}/\gamma_{calc} - 1$ for the series of RT₄Al₈ compounds.

Quantity	Ycalc	Yexp	λ	
YFe ₄ Al ₈	34 (Ref. 16)	60 (Ref. 26)	0.8	
LuFe ₄ Al ₈	33 (Ref. 16)	75 (Ref. 10)	1.3	
YMn ₄ Al ₈	18.4	95, ²⁷ 83 (Ref. 28)	4.2; 3.5	
LaMn ₄ Al ₈	20.5	265 (Ref. 28)	12	
YCr ₄ Al ₈	32.5	220 (Ref. 11)	5.8	
LaCr ₄ Al ₈	39.1	58 (Ref. 26)	0.5	
CeCr ₄ Al ₈	38.2	62, ²⁶ 180 (Ref. 29)	0.6; 4.7	

 χ ensures that the nonuniform distribution of the spin density in the unit cell and volume-correlation interaction effects²⁰ 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 RT₄Al₈ compounds is from exchange-enhanced spin paramagnetism, χ_{spin} . An approximate estimate of the parameters characterizing this contribution can be obtained using the Stoner model

$$\chi_{\rm spin} = \frac{\chi_P}{1 - \alpha \chi_P} \equiv S \chi_P, \tag{4}$$

where $\chi_P = \mu_B^2 N(E_F)$ 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 RT₄Al₈ compounds using the calculated χ_P and χ_{spin} are given in Table 6.

A comparison of the calculated values of χ_{spin} (Table 6) with theoretical values of the total susceptibility $\chi = \chi_{spin}$ $+ \chi_{orb}$ (Tables 3 and 4) shows that in the systems RMn₄Al₈ and RCr₄Al₈ studied here, the van Vleck orbital contribution χ_{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 χ_{orb} for CeCr₄Al₈ is about 20% of the total susceptibility and is determined mainly by the electronic states of the cerium atom, where the 4*f*-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 CeCr₄Al₈.

The experimental pressure dependences of χ for the RMn₄Al₈ and RCr₄Al₈ 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 $d \ln \chi/d \ln V$ corresponding to the dependences in Figs. 8 and 9. The tables show that the calculated $d \ln \chi/d \ln V$ are in good agreement with experimental data from the experiments on magnetic susceptibility under pressure. In addition, for the most studied system RMn4Al8, 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 $d \ln \chi/d \ln V \sim 20$. This estimate of the effect of chemical pressure is comparable to the calculated and experimental

TABLE 6. Calculated values of the parameters χ_P and χ_{spin} (10⁻³ cm³/mol), molecular field constant α (10⁻³ cm³/mol), and Stoner factor *S* of RT₄Al₈ compounds (for YFe₄Al₈ α is estimated using the Stoner criterion for magnetic ordering in Eq. (4), $\alpha \chi_P \geq 1$.

Quantity	χ _P	χspin	α	S
YFe ₄ Al ₈	0.880		≥1.1	
YMn ₄ Al ₈	0.252	4.04	3.72	16
LaMn ₄ Al ₈	0.282	13.3	3.47	47
YCr ₄ Al ₈	0.446	6.16	2.08	14
LaCr ₄ Al ₈	0.537	4.30	1.63	8
CeCr ₄ Al ₈	0.524	3.87	1.65	7.4



FIG. 10. Log-log plots of the experimental (\bigcirc) and calculated (\bullet) values of the magnetic susceptibility of RMn₄Al₈ compounds as functions of the unit cell volume (χ in units of 10^{-3} cm³/mol and V in (a.u.)³).

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 RMn₄Al₈ compounds.

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

$$\frac{d\ln\chi}{d\ln V} \simeq \frac{d\ln\chi_P}{d\ln V} + \alpha\chi \left(\frac{d\ln\alpha}{d\ln V} + \frac{d\ln\chi_P}{d\ln V}\right),\tag{5}$$

which is convenient for describing the temperature dependence of the magnetovolume effect determined mainly by the $\chi(T)$ dependence. Substituting the experimental values of $d\ln\chi/d\ln V$ at T = 300 K for YMn₄Al₈ (~37 according to our data) and for LaMn₄Al₈ (~55 (Ref. 14)), together with the calculated value $d\ln\chi_P/d\ln V \equiv d\ln N(E_F)/d\ln V \simeq 1.5$, yields a value for the volume derivative of the molecular field constant α in the RMn₄Al₈ compounds within a range of

$$\frac{d\ln\alpha}{d\ln V} = 0 - 0.3. \tag{6}$$

A similar value of the derivative $d\ln\alpha/d\ln V \sim 0.4$ follows from Eq. (5) for CeCr₄Al₈ when the corresponding experimental data for T = 78 K are used.

We note that for CeCr₄Al₈ the calculated value of the volume derivative of χ was roughly a factor of 1.5 smaller than the corresponding derivatives for the other RCr₄Al₈ compounds (Table 3). This appears to be related to the tetravalent state of the cerium ion in CeCr₄Al₈ and to the difference in the filling of the conduction band relative to the other RCr₄Al₈ systems, where the Y, La, and Lu ions are trivalent. The above data on a relatively weak volume dependence of α in the RMn₄Al₈ and RCr₄Al₈ systems are in sharp contrast with the typical values $d\ln\alpha/d\ln V \equiv d\ln J/d\ln V = -(0.7 - 1.5)$ for strong band paramagnetic materials^{30,31} and with the value

$$\frac{d\ln\alpha}{d\ln V} \simeq -2\tag{7}$$

for YFe_4Al_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 $\alpha \simeq 1.1 \times 10^3 \text{ mol/cm}^3$. One possible reason for the highly different and hard-toexplain 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_4Al_8 compounds,¹⁵ 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 RT₄Al₈, where R denotes a nonmagnetic 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 RT₄Al₈ family and that the magnetovolume effect $d\ln \chi/d\ln V$ is anomalously large in the RMn₄Al₈ and RCr₄Al₈ 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 3d-metals.

Refinement of the magnetic characteristics of the RT_4AI_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.

We thank I. D. Shcherbe and A. V. Terekhov for providing the samples of RT_4Al_8 .

This work was partially supported by the Slovak agency as part of VEGA Project No. 1/0145/13. The computational resources of the grid-cluster at the B. I. Verkin Institute of Lowtemperature Physics and Engineering of the National Academy of Sciences of Ukraine in Kharkov were used in this work.

a)Email: panfilov@ilt.kharkov.ua

- ³I. Felner and I. Nowik, J. Phys. Chem. Solids **39**, 951 (1978).
- ⁴I. Felner and I. Nowik, J. Phys. Chem. Solids 40, 1035 (1979).

¹K. H. J. Buschow, J. H. N. van Vucht, and W. W. van den Hoogenhof, J. Less-Common Met. **50**, 145 (1976).

²K. H. J. Buschow and A. M. van der Kraan, J. Phys. F: Met. Phys. 8, 921 (1978).

⁵W. Suski, in *Handbook on Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr. and L. Eyring (Elsevier, Amsterdam, 1996), Vol. 22, Chap. 149, p. 143.

Low Temp. Phys. 42 (6), June 2016

- ⁶J. A. Paixão, S. Langridge, S. Aa. Sorensen, B. Lebech, A. P. Gonçalves, G. H. Lander, P. J. Brown, P. Burlet, and E. Talik, *Physica B* **234–236**, 614 (1997).
- ⁷J. A. Paixão, M. Ramos Silva, J. C. Waerenborgh, A. P. Gonçalves, G. H. Lander, P. J. Brown, M. Godinho, and P. Burlet, Phys. Rev. B **63**, 054410 (2001).
- ⁸P. Schobinger-Papamantellos, K. H. J. Buschow, and C. Ritter, J. Magn. Magn. Mater. **186**, 21 (1998).
- ⁹C. Cardoso, T. Gasche, and M. Godinho, J. Phys.: Condens. Matter 18, 8817 (2006).
- ¹⁰A. M. Gurevich, V. M. Dmitriev, V. N. Eropkin, L. A. Ishchenko, N. N. Prenzlau, and L. V. Shlyk, Fiz. Nizk. Temp. **25**, 15 (1999) [Low Temp. Phys. **25**, 10 (1999)].
- ¹¹A. M. Gurevich, V. M. Dmitriev, V. N. Eropkin, B. Yu. Kotur, N. N. Prenzlau, V. Suski, A. V. Terekhov, and L. V. Shlyk, Fiz. Nizk. Temp. **27**, 1308 (2001) [Low Temp. Phys. **27**, 967 (2001)].
- ¹²H. Drulis, P. Gaczyński, W. Iwasieczko, W. Suski, and B. Ya. Kotur, Solid State Commun. **123**, 391 (2002).
- ¹³B. Andrzejewski, A. Kowalczyk, and T. Toliński, Acta Phys. Pol., A 109, 561 (2006).
- ¹⁴H. Nakamura, Y. Muro, S. Giri, J. Umemura, H. Kobayashi, T. Koyama, and T. Kohara, J. Phys. Soc. Jpn. 74, 2421 (2005).
- ¹⁵Y. Muro, H. Nakamura, and T. Kohara, J. Phys.: Condens. Matter 18, 3931 (2006).
- ¹⁶A. V. Logosha, G. E. Grechnev, A. A. Lyogenkaya, and A. S. Panfilov, Fiz. Nizk. Temp. **40**, 405 (2014) [Low Temp. Phys. **40**, 311 (2014)].
- ¹⁷P. Gaczyński, F. G. Vagizov, W. Suski, B. Kotur, W. Iwasieczko, and H. Drulis, J. Magn. Magn. Mater. 225, 351 (2001).
- ¹⁸H. Nakamura, S. Giri, and T. Kohara, J. Phys. Soc. Jpn. **73**, 2971 (2004).

- ¹⁹A. S. Panfilov, Fiz. Nizk. Temp. **41**, 1318 (2015) [Low Temp. Phys. **41**, 1029 (2015)].
- ²⁰G. E. Grechnev, Fiz. Nizk. Temp. **35**, 812 (2009) [Low Temp. Phys. **35**, 638 (2009)].
- ²¹J. M. Wills, M. Alouani, P. Andersson, A. Delin, O. Eriksson, and A. Grechnev, *Full-Potential Electronic Structure Method. Energy and Force Calculations with Density Functional and Dynamical Mean Field Theory*, Springer Series in Solid-State Sciences Vol. 167 (Springer Verlag, Berlin, 2010).
- ²²See http://fplmto-rspt.org/
- ²³See http://elk.sourceforge.net/
- ²⁴U. von Barth and L. Hedin, J. Phys. C: Solid State Phys. 5, 1629 (1972).
- ²⁵J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
- ²⁶I. H. Hagmusa, "Heat effects of magnetic phase transitions in intermetallic compounds," Ph.D. thesis (WZI, Amsterdam, 2000).
- ²⁷J. Y. Kim, J. G. Park, and B. K. Cho, J. Appl. Phys. **99**, 08F506 (2006).
- ²⁸I. H. Hagmusa, J. C. P. Klaasse, E. Brück, F. R. de Boer, and K. H. J. Buschow, J. Alloys Compd. **297**, 21 (2000).
- ²⁹H. Ido, T. Nishioka, and M. Kontani, J. Magn. Magn. Mater. **177–181**, 385 (1998).
- ³⁰A. S. Panfilov and I. V. Svechkarev, in Proceedings of the International Conference on the Physics of Transition Metals, Darmstadt, Germany (1992), Vol. 2, pp. 699.
- ³¹P. E. Brommer, G. E. Grechnev, J. J. M. Franse, A. S. Panfilov, Yu. Ya. Pushkar, and I. V. Svechkarev, J. Phys.: Condens. Matter 7, 3173 (1995).

Translated by D. H. McNeill