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Electronic structure and magnetic properties of RT_4Al_8 ($R = Sc, Y, La, Lu; T = Fe, Mn, Cr$) compounds. Hydrostatic pressure effects

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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 $3d$ -sublattice of the metal. The weak dependence of the magnetic properties on the element R shows up most clearly in the RFe_4Al_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 RFe_4Al_8 family is the detection of traces of a superconducting phase in the compounds $ScFe_4Al_8$ ($T_c = 6 K$), YFe_4Al_8 ($T_c = 6 K$), and $LuFe_4Al_8$ ($T_c \sim 24 K$) in studies of their surface resistivity and specific heat,^{10,11} well as in YFe_4Al_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 RFe_4Al_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 RMe_4Al_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 RMn_4Al_8 compounds is the significant influence of chemical pressure effects on their magnetism, as confirmed by an anomalously high dependence of the magnetic susceptibility $LaMn_4Al_8$ on external

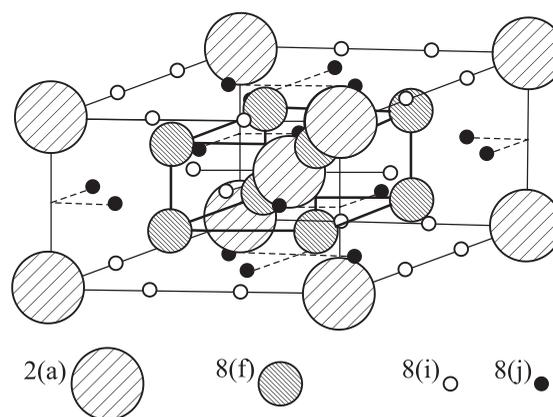


FIG. 1. The $ThMn_{12}$ structure into which the RT_4Al_8 compounds crystallize: the R atoms occupy 2(a) positions; the T atoms, 8(f) positions; and the Al atoms, two types of positions 8(i) and 8(j).

pressure.¹⁴ It is very important to take this factor into account when comparing the properties of the RMn_4Al_8 system and, perhaps, of the entire family of RT_4Al_8 compounds.

There is essentially no information on the magnetism of the RCr_4Al_8 compounds, except for some data on $\chi(T)$ for LuCr_4Al_8 over a narrow temperature range.⁴ The nature of the magnetic properties of the RT_4Al_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_4Al_8 and LuFe_4Al_8 .

In this paper we study the features of the electronic spectrum and magnetic properties of the RT_4Al_8 compounds with nonmagnetic elements $\text{R} = \text{Sc}, \text{Y}, \text{La},$ and Lu and their evolution over the series of $3d$ -metals ($\text{T} = \text{Cr}, \text{Mn},$ 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_4Al_8 and YMn_4Al_8 were measured at temperatures of 4–300 K with a SQUID magnetometer. The $\chi(T)$ curves measured for YFe_4Al_8 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 RFe_4Al_8 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 RFe_4Al_8 , the RMn_4Al_8 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 LaMn_4Al_8 and YMn_4Al_8 measured in a magnetic field of 10 kOe,¹⁴ along with our data for YMn_4Al_8 measured in a field of 0.2 kOe. ScMn_4Al_8 and LuMn_4Al_8 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 $C \approx 0.06 \text{ K cm}^3/\text{mol}$ for our sample

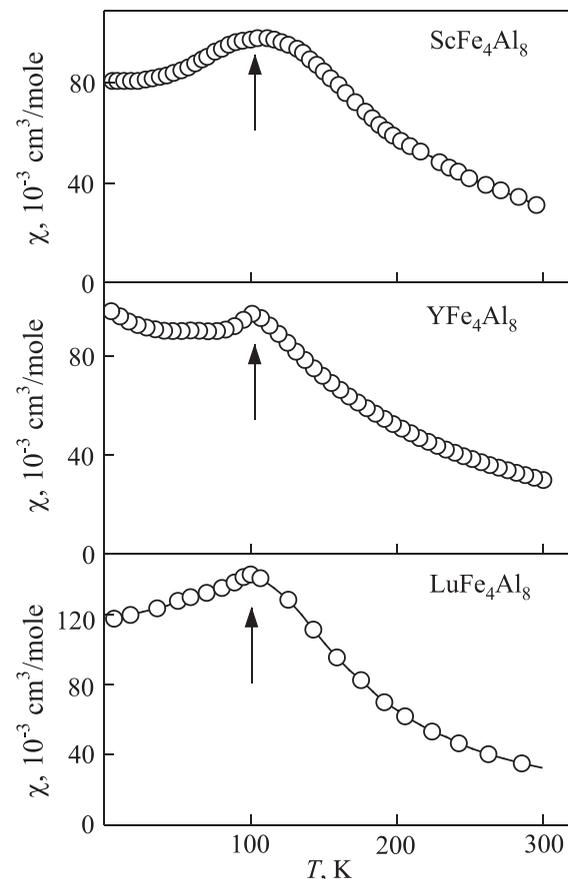


FIG. 2. Magnetic susceptibility as a function of temperature for YFe_4Al_8 (this paper), ScFe_4Al_8 ,¹⁷ and LuFe_4Al_8 .²

of YMn_4Al_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_4Al_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_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 YFe_4Al_8 , YMn_4Al_8 , and CeCr_4Al_8 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

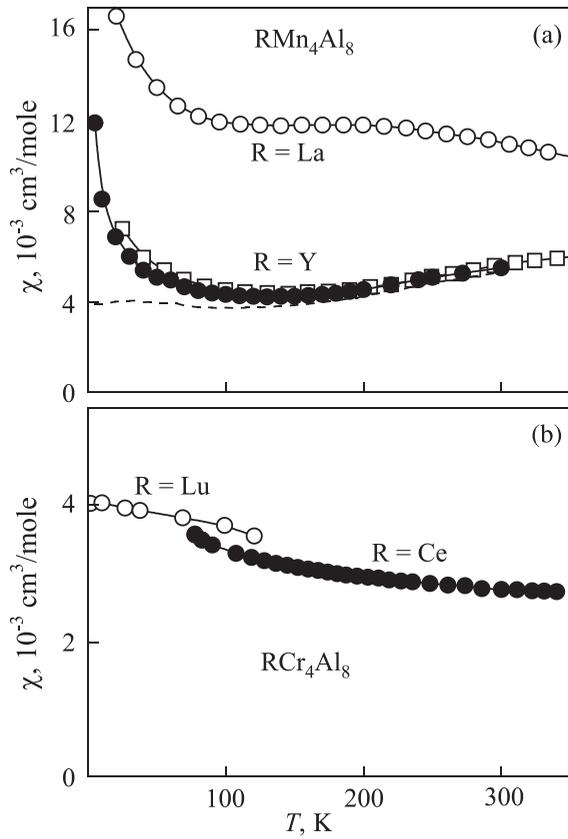


FIG. 3. Temperature dependences of the magnetic susceptibility for LaMn_4Al_8 (\circ)¹⁴ and YMn_4Al_8 (\square)¹⁴ and data from the present work for YMn_4Al_8 (\bullet); the dashed curve is corrected data with the low-temperature impurity contribution subtracted (see text for details) (a); (\circ) data 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 YMn_4Al_8 the table also lists the intrinsic susceptibilities $\chi_0 = \chi - C/T$ corrected for the impurity contributions and their baric derivatives, defined as $d \ln \chi_0 / dP = (\chi / \chi_0) d \ln \chi / dP$ 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 EIk²³). The exchange-correlation potential was included

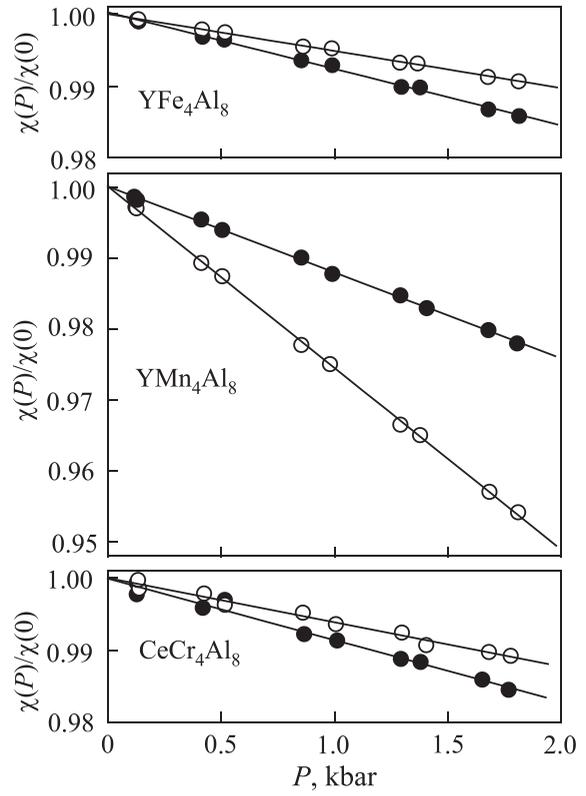


FIG. 4. Experimental plots of the magnetic susceptibility of several RT_4Al_8 compounds, normalized to the susceptibility at $P = 0$, as a function of pressure. The points (\circ) and (\bullet) correspond to temperatures of 300 and 78 K.

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 RT_4Al_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 1. Experimental values of the magnetic susceptibility χ ($10^{-3} \text{ cm}^3/\text{mol}$) and its baric derivative $d \ln \chi / dP$ (Mbar^{-1}) in RT_4Al_8 compounds, together with the corresponding values of these quantities for YMn_4Al_8 corrected for the impurity contribution, χ_0 and $d \ln \chi_0 / dP$ (see text for details).

Quantity	T (K)	YFe_4Al_8	YMn_4Al_8	CeCr_4Al_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
χ_0	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 RT_4Al_8 compounds in the sequence $T = Cr \rightarrow Mn \rightarrow Fe$. Calculated densities of states of the RT_4Al_8 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 $3d$ -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 Murnaghan equation

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

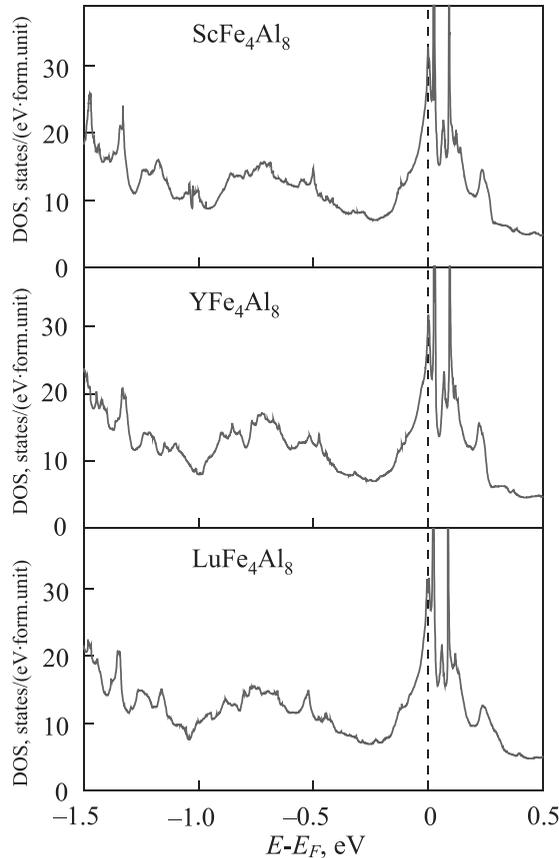


FIG. 5. Electron densities of state of RFe_4Al_8 ($R = Sc, Y,$ and Lu) compounds. The Fermi level at $E = 0$ is indicated by the vertical dashed line.

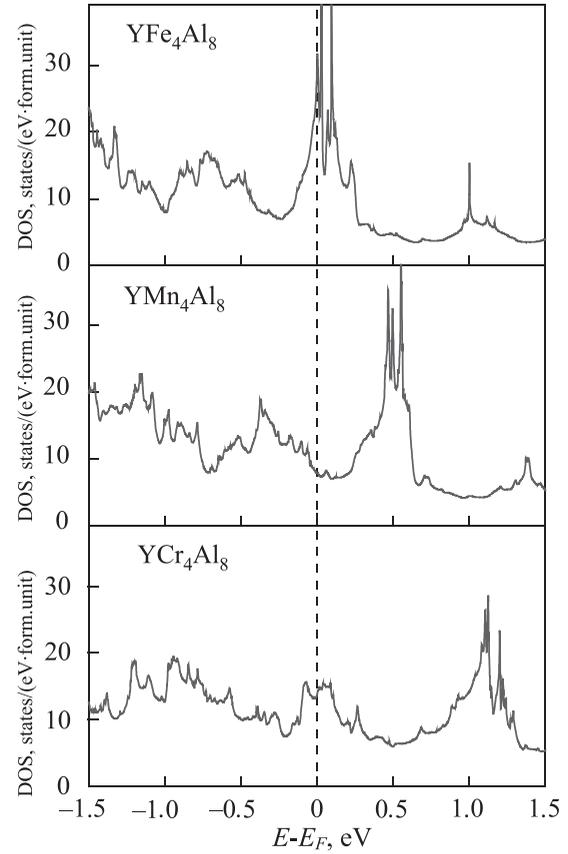


FIG. 6. Electron densities of state $N(E)$ of YT_4Al_8 ($T = Cr, Mn,$ and Fe) compounds.

where $B = B(V_0)$. The Murnaghan 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_4Al_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_4Al_8 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 \mathbf{H} by the FP-LMTO method.²⁰ Here the effect of the external magnetic field on the electronic

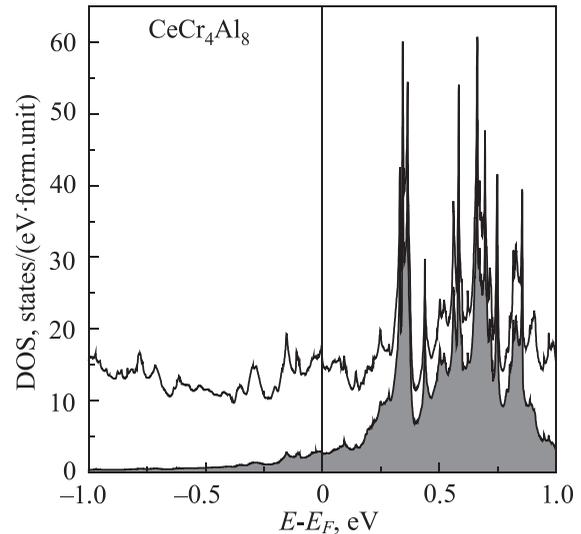


FIG. 7. Density of electronic states of the compound $CeCr_4Al_8$. The partial contribution of the $4f$ -state of cerium is indicated by the shaded region.

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 RT_4Al_8 .

Compound	$N(E_F)$	$d \ln N(E_F)/d \ln V$	B
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

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

in the FP-LMTO Hamiltonian, where $\hat{\mathbf{S}}$ is the spin operator and $\hat{\mathbf{I}}$ is the orbital angular momentum operator. The calculated induced spin and orbital magnetic moments in the external field \mathbf{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 RMn_4Al_8 and RCr_4Al_8 , 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 RMn_4Al_8 and RCr_4Al_8 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 RMn_4Al_8 and RCr_4Al_8 compounds are shown in Figs. 8 and 9. It should be noted that for the RFe_4Al_8 compounds the spin-polarized 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 RFe_4Al_8 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 RMn_4Al_8 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	~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 RCr_4Al_8 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 $T = Fe, Mn, \text{ and } Cr$ 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 RFe_4Al_8 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 RMn_4Al_8 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 RCr_4Al_8 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 RT_4Al_8 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

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

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

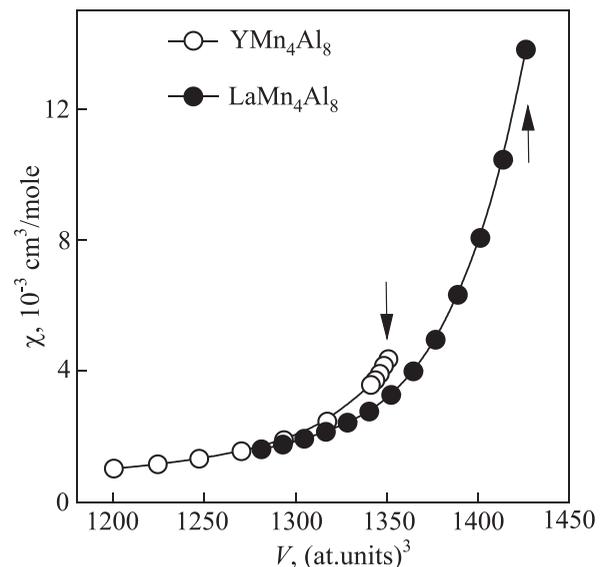


FIG. 8. Calculated dependences of the magnetic susceptibility of RMn_4Al_8 compounds on the unit cell volume. The arrows indicate the experimental values of the volume under normal conditions.

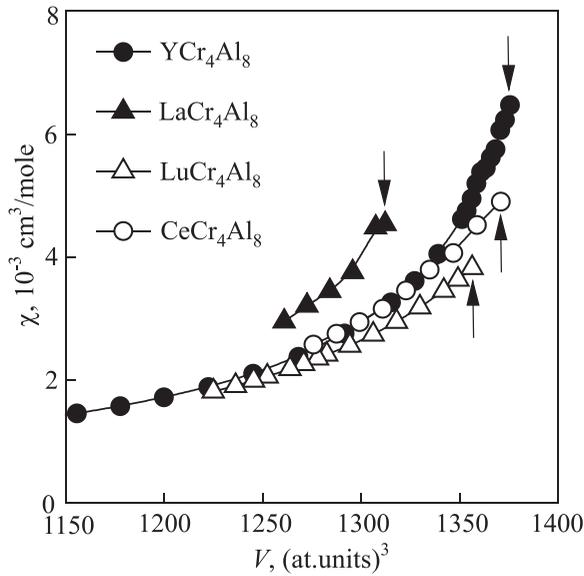


FIG. 9. Calculated dependences of the magnetic susceptibility of RCr_4Al_8 compounds on the unit cell volume. The arrows indicate the experimental values of the volume under normal conditions.

The values of γ_{calc} for YFe_4Al_8 and LuFe_4Al_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 γ_{exp} in Table 5 were also obtained for the AFM state of the YFe_4Al_8 and LuFe_4Al_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_4Al_8 and YFe_4Al_8 .^{10,11} However, the contribution to λ of the spin-fluctuation term λ_{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 $N(E_F)$.²⁰ The estimate of the electron-phonon renormalization $\lambda_{\text{el-ph}}$, therefore, remains unsettled, as does the origin of superconductivity in the RFe_4Al_8 compounds. We note also that the anomalously high γ_{exp} observed in some compounds, such as LaMn_4Al_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_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 $\text{mJ/mol}\cdot\text{K}^2$) and of the parameter $\lambda = \gamma_{\text{exp}}/\gamma_{\text{calc}} - 1$ for the series of RT_4Al_8 compounds.

Quantity	γ_{calc}	γ_{exp}	λ
YFe_4Al_8	34 (Ref. 16)	60 (Ref. 26)	0.8
LuFe_4Al_8	33 (Ref. 16)	75 (Ref. 10)	1.3
YMn_4Al_8	18.4	95, ²⁷ 83 (Ref. 28)	4.2; 3.5
LaMn_4Al_8	20.5	265 (Ref. 28)	12
YCr_4Al_8	32.5	220 (Ref. 11)	5.8
LaCr_4Al_8	39.1	58 (Ref. 26)	0.5
CeCr_4Al_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 RT_4Al_8 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

$$\chi_{\text{spin}} = \frac{\chi_P}{1 - \alpha\chi_P} \equiv S\chi_P, \quad (4)$$

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 RT_4Al_8 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 $\chi = \chi_{\text{spin}} + \chi_{\text{orb}}$ (Tables 3 and 4) shows that in the systems RMn_4Al_8 and RCr_4Al_8 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 CeCr_4Al_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_4Al_8 .

The experimental pressure dependences of χ for the RMn_4Al_8 and RCr_4Al_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 $d\ln\chi/d\ln V$ 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 RMn_4Al_8 , the calculated data correlate with the dependence of the magnetic susceptibility in the sequence $\text{R} = \text{Sc}, \text{Y}, \text{La}, \text{and Lu}$ 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} ($10^{-3} \text{ cm}^3/\text{mol}$), molecular field constant α ($10^{-3} \text{ cm}^3/\text{mol}$), and Stoner factor S of RT_4Al_8 compounds (for YFe_4Al_8 α is estimated using the Stoner criterion for magnetic ordering in Eq. (4), $\alpha\chi_P \geq 1$).

Quantity	χ_P	χ_{spin}	α	S
YFe_4Al_8	0.880	...	≥ 1.1	...
YMn_4Al_8	0.252	4.04	3.72	16
LaMn_4Al_8	0.282	13.3	3.47	47
YCr_4Al_8	0.446	6.16	2.08	14
LaCr_4Al_8	0.537	4.30	1.63	8
CeCr_4Al_8	0.524	3.87	1.65	7.4

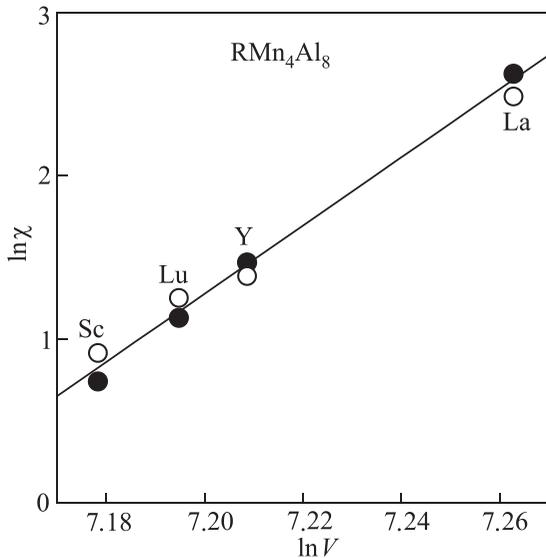


FIG. 10. Log-log plots of the experimental (○) and calculated (●) values of the magnetic susceptibility of RMn_4Al_8 compounds as functions of the unit cell volume (χ in units of $10^{-3} \text{ cm}^3/\text{mol}$ and V in (a.u.)³).

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 RMn_4Al_8 compounds.

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

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

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 $T = 300 \text{ K}$ for YMn_4Al_8 (~ 37 according to our data) and for LaMn_4Al_8 (~ 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 RMn_4Al_8 compounds within a range of

$$\frac{d\ln\alpha}{d\ln V} = 0 - 0.3. \quad (6)$$

A similar value of the derivative $d\ln\alpha/d\ln V \sim 0.4$ follows from Eq. (5) for CeCr_4Al_8 when the corresponding experimental data for $T = 78 \text{ K}$ are used.

We note that for CeCr_4Al_8 the calculated value of the volume derivative of χ was roughly a factor of 1.5 smaller than the corresponding derivatives for the other RCr_4Al_8 compounds (Table 3). This appears to be related to the tetravalent state of the cerium ion in CeCr_4Al_8 and to the difference in the filling of the conduction band relative to the other RCr_4Al_8 systems, where the Y, La, and Lu ions are trivalent. The above data on a relatively weak volume dependence of α in the RMn_4Al_8 and RCr_4Al_8 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

$$\frac{d\ln\alpha}{d\ln V} \simeq -2 \quad (7)$$

for YFe_4Al_8 given by Eq. (5) with the corresponding experimental values of $d\ln\chi/d\ln V$ for $T = 300 \text{ K}$ 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-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 $3d$ -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 RT_4Al_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_4Al_8 family and that the magnetovolume effect $d\ln\chi/d\ln V$ is anomalously large in the RMn_4Al_8 and RCr_4Al_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 $3d$ -metals.

Refinement of the magnetic characteristics of the RT_4Al_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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