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Journal of Alloys and Compounds 262-263 (1997) 65-70

Journal of ALLOYS AND COMPOUNDS

Electronic and magnetic structure of ternary transition metal arsenides related to the Fe_2X type ($X = P$, As)

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Abstract

The spin-polarized KKR-CPA band structure calculations were done by KKR-CPA method on $Mn_{2-x}Cr_xAs$ series [both in ferromagnetic (FM) and anti-ferromagnetic (AFM) state], guided by the neutron diffraction measurements on CrMnAs. Our results show a specific evolution of the electronic structure. Going from AFM Mn_2As to AFM CrMnAs, we found that the magnetic moments on Cr-atoms change a sign, crossing zero-value near $x \approx 0.5$. For the hexagonal CrNiAs compound, the present KKR results, reveal a significant effect of lattice parameters on magnetic properties. Computed a and c lattice constants by minimizing total energy are 2-3% smaller than found in a new neutron diffraction experiment (at $T = 117$ K). Generally, our computations of the magnetic moments are in quite good agreement with values deduced from neutron data. © 1997 Elsevier Science S.A.

Keywords: Electronic structure; Magnetic structure; 3d ternary arsenides; Neutron diffraction measurements

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1. Introduction

Phosphides and arsenides of transition metals with formula MM'X usually crystallize in three different crystal structure types: hexagonal $P\bar{6}2m$, tetragonal $P4/nmm$ or orthorhombic $Pnma$. All these structures contain two common blocks, tetrahedral (T) and pyramidal (P) sites, which form the coordination of the metal atoms [1,2]. In M_2X (M = Cr, Mn, Fe, Co and X = As, P) compounds, magnetic moments on atoms located in pyramidal sites always have a larger value than those in tetrahedral positions. The M_2X compounds exhibit a variety of magnetic structures, which depend on crystal structure as well as constituent atoms [3]. For instance, the tetragonal Fe_2As is anti-ferromagnetic, which the hexagonal Fe_2P shows a ferromagnetic state [4]. In most cases, the M_2P compounds show ferro- or ferrimagnetic ordering, while the M_2As systems are anti-ferromagnets. Solid solutions alloying end compounds sometimes exhibit ordering characteristics, which can be related to the magnetic structure of both parent compounds. Such a behavior, when compared with Mn_2As and Cr_2As, was observed from the neutron diffraction analysis of the CrMnAs compound [5], and inspired our band structure computations of $Mn_{2-x}Cr_xAs$ series.

In the hexagonal $Cr_{2-x}Ni_xAs$ system, a ferromagnetic component appears in the vicinity of the CrNiAs composition ($x \approx 1.0$), while apart from this range more complex magnetic structures occur [6]. The appearance of ferromagnetism is associated with a strong change in the cell parameters. The effect of lattice constants variation on magnetic behaviors in this compound is discussed in conjunction with the band structure calculations.

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0925-8388/97/$17.00
PII S0925-8388(97)00330-7

In comparison with the above-mentioned systems the tetragonal VMnAs is considered, where only Mn atoms display magnetic moments.

2. The KKR–CPA method

We implemented and carried out the full charge and spin self-consistent calculations by the Korringa–Kohn–Rostoker (KKR) method (without any adjustable parameters) on ordered as well as on disordered systems with the use of the coherent potential approximation (CPA) [7–9]. For all compounds as well as alloys, the muffin-tin potentials were constructed within the local spin density approach, employing the exchange-correlation part of the Barth–Hedin form [10]. For the final potentials, the total density of states (DOS), site-decomposed component DOS, as well as l-decomposed (with $l_{max} = 2$) partial DOS were computed. The integration in k-space (using 85 k-points in the irreducible part of the Brillouin zone) was performed by the tetrahedron method as described in Kaprzyk and Mijnarends [11].

We used the KKR–CPA code with the generalized Lloyd formula [7] and the complex energy plane integration techniques on elliptic contour when computing spin-polarized charge densities [8,9].

The experimental lattice constants and atomic positions used in our band structure calculations are listed in Table 1, apart from the CrNiAs compound (see, Sec. 3.2). Since the lattice constants of Mn_2As and CrMnAs are very close, we took the positional parameters for the $Mn_{2-x}Cr_xAs$ ($0 < x < 1$) alloys by interpolating them between border values.

3. Results and discussion

3.1. $Mn_{2-x}Cr_xAs$ $0 < x < 1$

The $Mn_{2-x}Cr_xAs$ system keeps a P4/*nmm* structure in the whole range of x, but various types of anti-ferromagnetic (AFM) orderings occur when comparing Cr_2As, CrMnAs and Mn_2As and compounds (see, Fig. 1). The neutron studies of the CrMnAs [5] showed that, Cr(T) magnetic moments are arranged as Cr(T) in Cr_2As, while Mn(P) magnetic moments are coupled as Mn(P) in Mn_2As.

The aim of the electronic structure study of AFM $Mn_{2-x}Cr_xAs$, was to detect the change of magnetic ordering when passing from Mn_2As to CrMnAs. The spin-polarized KKR–CPA calculations were performed in the unit cell doubled along the c axis (containing four formula units). Experimental results [5] show that Cr atoms in CrMnAs system dominantly occupy ($\approx 80\%$) tetrahedral sites. In the KKR–CPA calculations of $Mn_{2-x}Cr_xAs$, we assumed, that Cr atoms are distributed only on tetrahedral sites.

The results for the concentrations $x = 0.0$ and $x = 1.0$ give one-impurity properties of Cr(3f) in Mn_2As and Mn(3f) in CrMnAs, respectively.

In Fig. 2, the variations of the magnetic moments (on T_1, T_2 and P_1, P_2 sites) in $Mn_{2-x}Cr_xAs$ are presented. The total magnetization per unit cell is zero for the whole range of x, as a consequence of AFM ordering. Interestingly, the composition dependence measurements of T_N [14] show a discontinuity at $x = 0.6$, close to the point where we detected zero-value of magnetic moment on Cr atoms. At this content we have sign changing of the spin-polarization of electrons on Cr-sublattices.

In Fig. 3 we present the densities of states spectra in anti-ferromagnetic Mn_2As, CrMnAs and Cr_2As compounds. From the component DOS one can see the polarization of electronic states on non-equivalent tetrahedral and pyramidal sites (T_1, P_1, T_2 and P_2) that results in the following values of magnetic moments (in μ_B) −0.43, 1.76, 0.43, −1.76 in Cr_2As; −0.62, −2.96, 0.62, 2.96 in CrMnAs and 1.77, −3.57, −1.77, 3.57 in Mn_2As. The above-mentioned KKR-results are slightly different than the end-point values presented in Fig. 2, since only the positional parameters were changed in the KKR-CPA computations.

The calculated magnetic moments are in satisfying agreement with the following neutron diffraction data: 0.40 μ_B, 1.34 μ_B [13] for Cr_2As and 0.83 μ_B, 2.97 μ_B

Table 1
Lattice parameters and atomic positions used in the KKR calculations

Compound	Space group	a (Å)	c (Å)	Tetrahedral site	Pyramidal site	
Cr_2As	P4/*nmm*	3.594	6.346	Cr	Cr ($z = 0.325$)	As ($z = 0.725$)
CrMnAs	P4/*nmm*	3.758	6.259	Cr	Mn ($z = 0.316$)	As ($z = 0.720$)
Mn_2As	P4/*nmm*	3.786	6.264	Mn	Mn ($z = 0.330$)	As ($z = 0.735$)
VMnAs	P4/*nmm*	3.722	6.483	V	Mn ($z = 0.351$)	As ($z = 0.727$)
CrNiAs	$P\bar{6}2m$	6.108	3.656	Ni ($x = 0.251$)	Cr ($x = 0.573$)	—

In tetragonal systems (P4/*nmm* type) presented below, atoms occupy tetrahedral (2a): [0,0,0] and pyramidal (2c): [1/2, 0, z] positons. In the hexagonal CrNiAs ($P\bar{6}2m$ type) Ni atoms occupy tetrahedral (3f): [x,0,0], Cr atoms occupy pyramidal (3g): [x,0,1/2] positions, while As atoms occupy (2c):[1/3,2/3,0] and (1b):[0,0,1/2] sites.

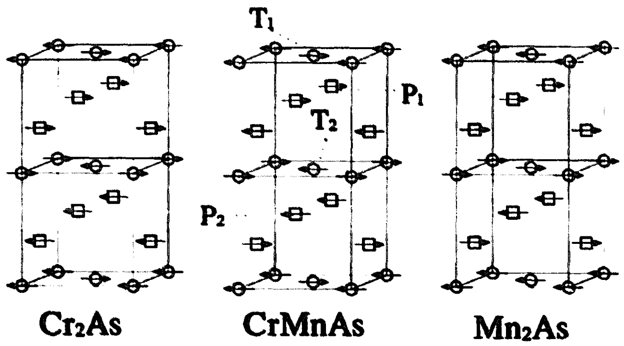

Fig. 1. The schematic magnetic structures of the Mn_2As, CrMnAs and Cr_2As compounds. The tetrahedral (T) and pyramidal (P) positions are marked by circles and squares, respectively. The T_1, T_2 and P_1, P_2 denote inequivalent tetrahedral and pyramidal positions in the doubled unit cell along the c-axis.

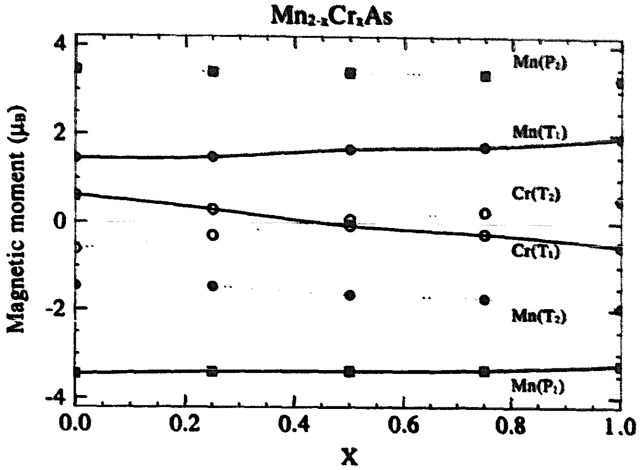

Fig. 2. Atomic magnetic moments variations in $Mn_{2-x}Cr_xAs$ ($0 < x < 1$).

[5]; 0.4 μ_B, 3.1 μ_B [14] for CrMnAs (see also Table 2). In fact, for the CrMnAs sample, the effective magnetic moments on P and T sites were measured, accounting for a certain Mn–Cr disorder detected in the experiment [5]. As far as the Mn_2As system is concerned, the KKR computations give the magnetic moments on T and P sites 1.77 μ_B and 3.57 μ_B, respectively, which are close to the experimental values 1.8 μ_B, 3.4 μ_B (at room temperature) and 2.2 μ_B, 4.1 μ_B (at liquid-nitrogen temperature) [15]; but the computed magnetic moment on T-sites given above is quite far from 3.5 μ_B measured in Austin et al. [16].

As it was previously shown for the system Fe_2P in [4], the use of our ab initio magnetic form factors in the refinements of neutron diffraction data may result in better agreement between computed and observed atomic magnetic moments.

3.2. CrNiAs

In the hexagonal $Cr_{2-x}Ni_xAs$ system, the appearance of ferromagnetism is associated with strong changes in the cell parameters (c goes to a maximum and a decreases smoothly with x) [6]. Thus, we performed our band structure calculations for a few different values of a and c. Otherwise, the estimated magnetic moments both of chromium (P) and nickel (T) may deviate markedly from the respective values deduced from neutron diffraction and magnetization measurements [5].

In Fig. 4 we show the total energy E_{tot} of the CrNiAs (in ferromagnetic ground state) as a function of a and c lattice constants. The equilibrium values a_{eq} and c_{eq} derived from the two-dimensional $E(a,c)$ plot are 5.92 Å and 3.54 Å, respectively. These values are smaller than the experimental data, $a = 6.108$ Å and $c = 3.656$ Å, observed at RT (see, Table 1). Recent refinements of new neutron diffraction data collected at $T = 117$ K for the CrNiAs sample give the lattice constants $a = 6.069$ Å and $c = 3.626$ Å in better agreement. In our total energy analysis the positional parameters were not changed, which may give the rise to an additional discrepancy. We are not aware of any temperature dependence measurements of x(3f) and x(3g).

Interestingly, with our a_{eq} and c_{eq}, the KKR computations give the magnetization per formula unit $\mu_{th} = 1.31$ μ_B, which is close to the measured value $\mu_{exp} = 1.22$ μ_B. In Fig. 5 we present the variations of the magnetic moment on Cr site vs. c parameters at three values of the a lattice constant. In contrast to the strong influence of a and c values on the μ_{Cr}, this effect is not so pronounced as far as the μ_{Ni} is concerned. The value of the magnetic moment on Ni site changes between 0.05 and 0.20 μ_B.

If comparing the magnetic moments in CrNiAs from the neutron diffraction measurements [5] $\mu_{Cr} = 0.65$ μ_B and $\mu_{Ni} = 0.55$ μ_B, with the KKR results at the RT lattice data ($a = 6.108$ Å and $c = 3.656$ Å) we find $\mu_{Cr} = 2.50$ μ_B and $\mu_{Ni} = 0.16$ μ_B in striking difference. When looking at these magnetic moments at computed a_{eq} and c_{eq} lattice data, we get $\mu_{Cr} = 1.23$ μ_B and $\mu_{Ni} = 0.12$ μ_B. Although the agreement with the neutron data cited above is much improved, it is not very satisfactory. If looking at the DOS of CrNiAs at Ni(3f) position (3rd column in Fig. 6) we find its value at E_F relatively small, unlike what one can expect from experimental $\mu_{Ni} = 0.55$ μ_B.

If comparing our results on CrNiAs with the previous LMTO calculations [12], we find close agreement when considering magnetic moments (see, Table 2) and DOS-shapes (3rd column in Fig. 6), however, the equilibrium lattice constant ($a = 5.92$ Å) from our KKR-method is slightly smaller than $a = 5.975$ Å (c-value not reported) from Ishida et al. [12].

The above presentation shows that the magnitude

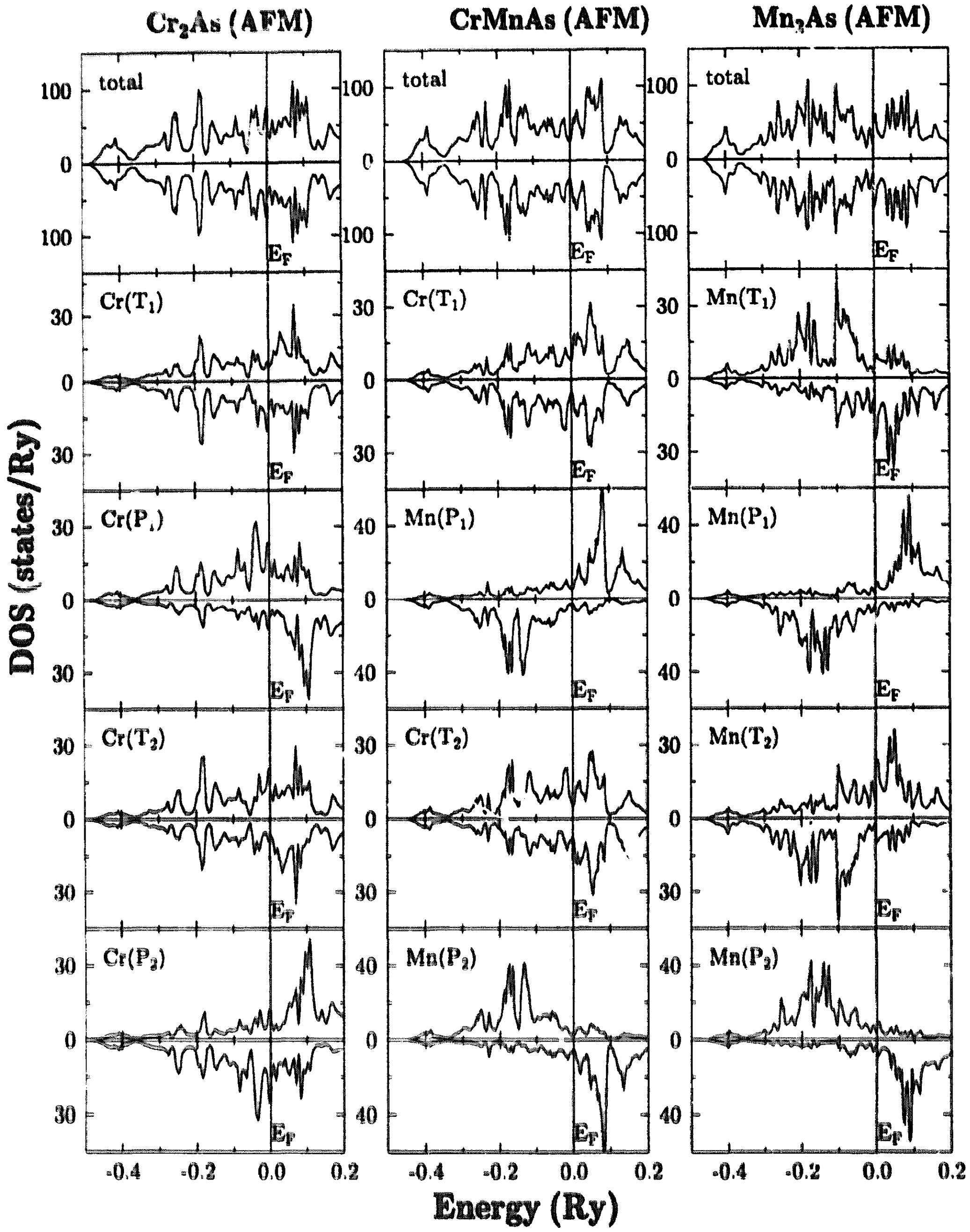

Fig. 3. Densities of states (total and component) of the Cr_2As (1st column), the CrMnAs (2nd column) and the Mn_2As (3rd column) in AFM state.

of the magnetic moments, particularly on Cr atoms, is very sensitive to the change of a and c lattice constants. Thus the future theoretical and experimental studies of such system based on CrNiAs, should also focus on the magneto-elastic properties.

3.3. VMnAs

The tetragonal VMnAs (fully ordered phase), where the one electron is 'removed' due to replacing Cr with V at the tetrahedral site, show AFM ordering of magnetic moments on Mn atoms. Both calculations and experiments give a zero magnetic moment on the V site, that was found in many other transition element compounds containing vanadium. The low value of DOS at E_F on V-site (see, 2nd column in Fig. 6) is not sufficient to fulfil the local Stoner's criterion and may explain the zero-value of V magnetic moment. When looking at the Mn-site we find a very strong spin-polarization with a resulting magnetic moment, 3.33 μ_B (in FM state) or slightly less, 3.25 μ_B from the computations carried out assuming AFM ordering.

Table 2
Magnetic moments on pyramidal and tetrahedral sites in mentioned arsenides: comparison between neutron diffracton measurements data and the KKR band structure results

Compound	Magnetic moments				
	Total	T-site		P-site	
		Neutron	KKR	Neutron	KKR
Cr_2As	0.0	0.40^a	0.43	1.34^a	1.75
CrMnAs	0.0	0.83^b	0.63	2.97^b	2.96
	—	0.4^c	—	3.1^c	—
Mn_2As	0.0	$1.8\ (2.1)^d$	1.77	$3.4\ (4.1)^d$	3.57
	—	3.5^e	—	3.7^e	—
VMnAs	0.0	0.0^b	0.0	3.12^b	3.25
CrNiAs	1.22^b	0.65^b	1.23	-0.55^b	0.12
	—	—	1.19^f	—	0.11^f

[a] [13].
[b] [5].
[c] [14].
[d] [15].
[e] [16].
[f] [12] LMTO–ASA method.

4. Conclusions

From the comparison of the above-mentioned systems, we conclude that the magnitude of magnetic moments as well as the type of magnetic ordering strongly depend on a substituted metal and distances between atoms. In the $Mn_{2-x}Cr_xAs$ series, the Mn–Mn distance seems to be important in the formation of different types of AFM ordering. On substituting Mn by Cr in $Mn_{2-x}Cr_xAs$, a systematic change of polarization of Cr(T) DOS was found, which resulted in the change of the mutual alignment of the magnetic moments on tetrahedral and pyramidal sites. In that sense, from ab initio KKR–CPA calculations we observe the specific evolution of the electronic and magnetic structure when passing from the Mn_2As to the CrMnAs compound. The similar effect on densities of states can be expected in Cr-rich $Mn_{2-x}Cr_xAs$ ($1 < x < 2$) alloys, where the magnetic ordering on pyramidal sites becomes similar to that of the Cr_2As.

From the densities of states in the AFM CrMnAs (see, 2nd column in Fig. 3), we observe, that E_F lies in a valley between DOS-peaks. The calculated DOS of the CrMnAs in the ferromagnetic state (see, 1st column in Fig. 6) show drastic differences between densities of states at E_F for spin-up and spin-down electrons. One then can expect interesting magnetotransport properties.

In the CrNiAs compound the KKR results show a strong influence of the a and c lattice constants on the magnitude of calculated magnetic moments. This must be taken into account for a fair comparison of band theory and neutron results. Further experimental and theoretical studies were undertaken to get more insight into the magnetic and crystal phases of $Cr_{2-x}Ni_xAs$.

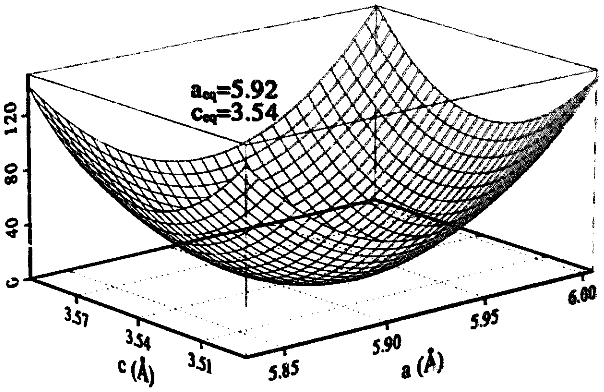

Fig. 4. The total energy E_{tot} (relatively to the E_{tot} in minimum) of the ferromagnetic CrNiAs vs. a and c lattice constants derived from the KKR computations.

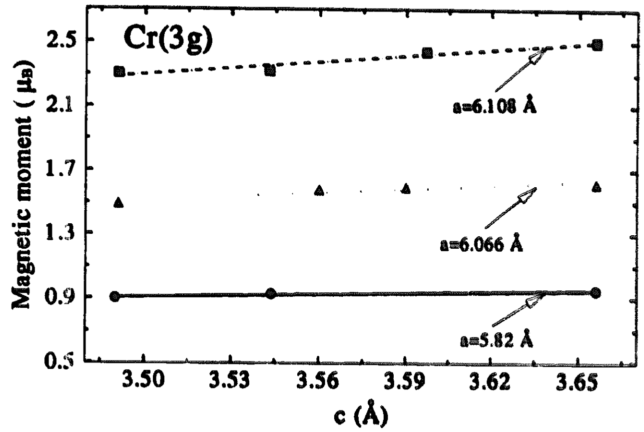

Fig. 5. The calculated magnetic moment on the Cr(3g) site in the hexagonal CrNiAs for various a and c lattice constants.

The understanding of magnetic properties of VMnAs, as observed in neutron diffraction measurements and resulting from the KKR-computations is quite satisfactory, with magnetic moments agreement on V and Mn sites.

Acknowledgements

This work was partly performed at CNRS Grenoble, during the TEMPRA project granted for J.T. from the Rhône-Alpes Region Foundation.

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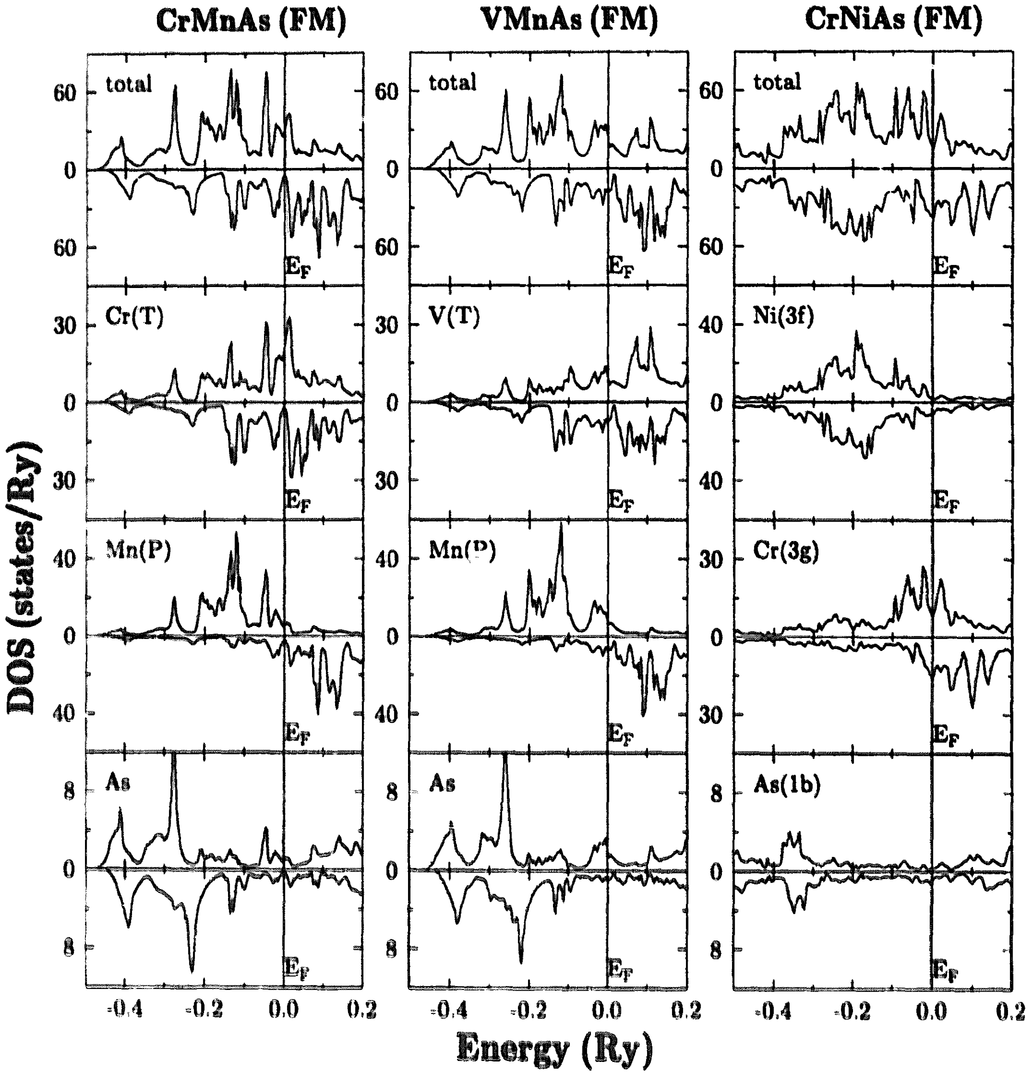

Fig. 6. Densities of states of the CrMnAs (1st column), the VMnAs (2nd column) and the CrNiAs (3rd column), all in FM state. The DOS of the CrNiAs correspond to the computations at a_{eq} and c_{eq}.

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