

Research Article

Antiferromagnetic Phase Transition in Cr_2As via Anisotropy of Exchange Interactions

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The electronic structure of antiferromagnetic Cr_2As is investigated. Anisotropy of exchange interactions between chrome sublattices is determined ($J^X(\text{Cr}_I - \text{Cr}_{II}) = 4.77$ meV, $J^Y(\text{Cr}_I - \text{Cr}_{II}) = -6.36$ meV). The behavior of exchange integrals from the magnetic structure is analyzed.

1. Introduction

Intermetallic compounds of 3d metals with As or Sb possessing a tetragonal crystal structure of the Cu_2Sb type (space symmetry group D_{4h}^7 -P4/nmm) have garnered a significant interest from the research community for their diverse magnetic structures. For example, Mn_2Sb is a ferrimagnet [1], and Mn_2As [2], Fe_2As [3], and Cr_2As [4] are antiferromagnets. The antiferromagnetic phase of Cr_2As is distinguished by two aspects: the small magnetic moments (in terms of the Bohr magneton) of the atoms ($M(\text{Cr}_I) = 0.4_B$, $M(\text{Cr}_{II}) = 1.34_B$ [4]) and its magnetic structure (Figure 1(b)). The peculiarity of the latter is that the effective molecular field between the Cr_I and Cr_{II} subsystems is compensated in the isotropic exchange approximation. This should lead to uncorrelated ordering of both subsystems, i.e., to the existence of two transition temperatures.

Initially, experimental studies revealed only one critical temperature ($T_N = 393$ K) [4], which led to the conclusion that the anisotropic exchange interaction of Cr_I - Cr_{II} was significant [5]. However, later, in [6], a second critical temperature was detected (Figure 2, $T_t = 175$ K) corresponding to the ordering of the Cr_I subsystem. Thus, the anisotropic part of the Cr_I - Cr_{II} exchange interaction is not crucial and “works” only in the region of $T_t < T < T_N$, inducing a small magnetic moment of Cr_I (Figure 2). Thus,

ab initio calculation and subsequent analysis of the electronic structure and interatomic exchange integrals in Cr_2As are of interest to us.

2. Crystal Structure and Electronic Structure of Cr_2As

The basic parameters of the crystal and magnetic structures were taken from the experiment [4, 6]. Cr_2As has a Cu_2Sb -type tetragonal crystal structure with the symmetry group D_{4h}^7 -P4/nmm, $a = 3.60$ Å, and $c = 6.34$ Å. Cr_I occupies the positions of the $2a(0, 0, 0)$ type, and Cr_{II} and As occupy positions of the $2c(0, 0.5, z)$ type with parameters $z_{\text{Cr}} = 0.325$ and $z_{\text{As}} = 0.725$, respectively. We considered all ten collinear magnetic structures (Table 1), but the calculation was converged only for four of them (Table 2). The magnetic moment of a specific atom at position \mathbf{r}_0 is given by [7]: $M_{[0,1,0]}(\mathbf{r}_0) \sim (\delta E(\mathbf{r}_0)/J_0)\mu_B$, where $\delta E = \int^{E_F} d\epsilon \epsilon (\text{LDOS}_\uparrow(\mathbf{r}_0, \epsilon) + \text{LDOS}_\downarrow(\mathbf{r}_0, \epsilon))$ and J_0 is a single-center exchange integral discussed in detail in the next section. Calculations of the electronic structure and exchange integrals in Cr_2As are performed by fully relativistic Korringa-Kohn-Rostoker method (SPR-KKR software package [8]). The atomic sphere approximation was used for the crystal potential. The exchange-correlation energy was calculated in the local density approximation without gradient corrections [9].

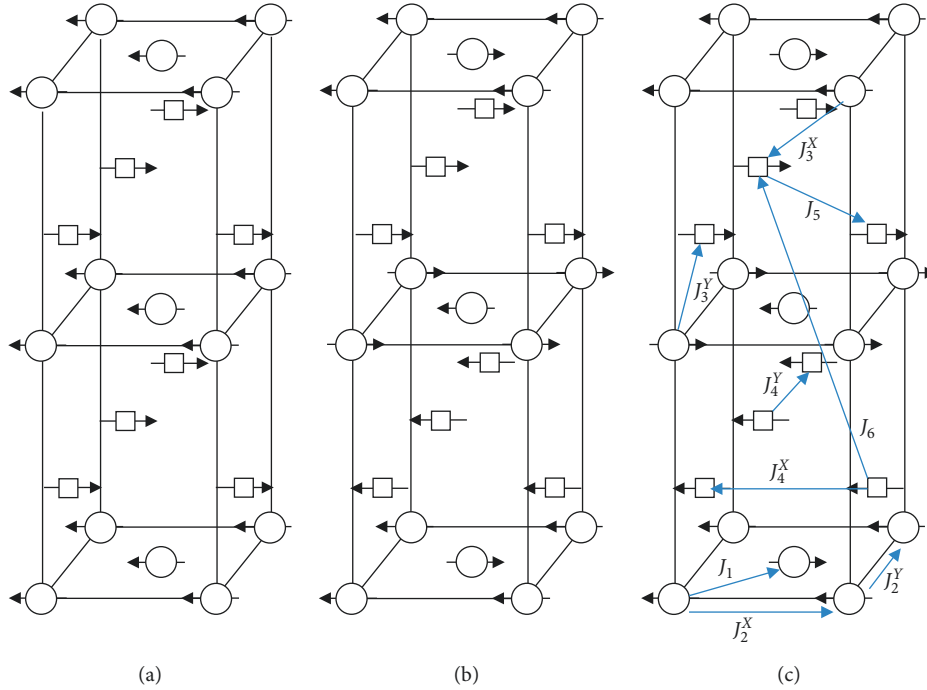


FIGURE 1: Magnetic structure of Cr_2As : FIM (a) and AF (b). \circ and \square indicate Cr_I and Cr_{II} , respectively. Only metal atoms are shown. (c) Main interatomic exchange interactions.

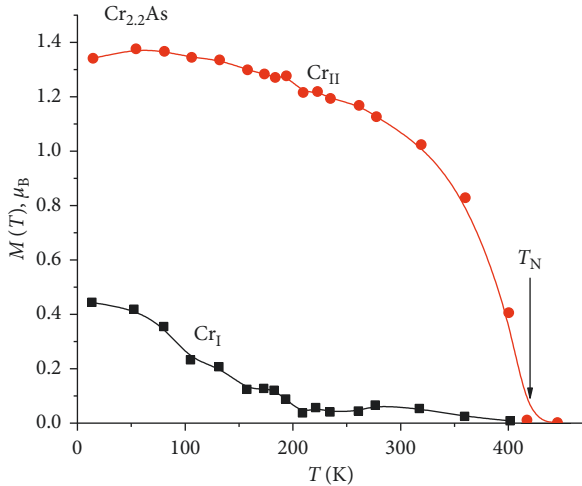


FIGURE 2: Temperature dependence of the sublattice magnetization of Cr (\circ) and Cr_{II} (\bullet)[6].

According to the results of calculations, the lowest energy has an antiferromagnetic structure AF3 (Table 2, Figure 1(b)), which agrees with the experimental data. At the same time, the calculation shows the instability of the ferromagnetic phase. Therefore, as a starting point, a ferrimagnetic structure of the Mn_2Sb type was considered (Figure 1(a)).

The electronic structure of nonmagnetic Cr_2As is shown in Figure 3, and its magnetic counterpart is depicted in Figure 4. The conduction band is located above 0.25 Ry and is formed mainly by the 3 d states of Cr and 4 p states of As that indicates strong $p-d$ hybridization in this compound.

In general, the electronic structure is typical for pnictides of transition metals and agrees with the results of other authors [10]. The Cr_2As compound is a metal, and all features of the magnetism of transition metal compounds are inherent in it. Chromium d -electrons create magnetic and transport properties. They are delocalized and so are the magnetic moments of chromium atoms (Table 2).

The magnetic moments of chromium in the ferrimagnetic ($M(\text{Cr}_I) = 0.709\mu_B$, $M(\text{Cr}_{II}) = 1.438\mu_B$) and antiferromagnetic (AF3, $M(\text{Cr}_I) = 0.937\mu_B$, $M(\text{Cr}_{II}) = 1.633\mu_B$) phases agree with the experimental data [4] ($M(\text{Cr}_I) = 0.4\mu_B$, $M(\text{Cr}_{II}) = 1.34\mu_B$) and the results of other calculations by LAPW [10] ($M(\text{Cr}_I) = 0.33\mu_B$, $M(\text{Cr}_{II}) = 1.37\mu_B$) and KKR [11] ($M(\text{Cr}_I) = 0.43\mu_B$, $M(\text{Cr}_{II}) = 1.75\mu_B$) methods. The high value of the Cr_I magnetic moment is related to the used approximation for potential of crystal lattice [11].

3. Interatomic Exchange Interactions and Critical Magnetization Temperature

The interatomic exchange integrals were calculated by the method [12], based on the calculation of the second derivative of the total energy functional from the deviations of the selected pair of spins from equilibrium. The effective classical Heisenberg Hamiltonian for metals/alloys is as follows:

$$H = -\frac{1}{2} \sum_{i \neq j} [(J_{ij}^{\text{iso}} + J_{ij}^{\text{sym}}) \mathbf{e}_i \cdot \mathbf{e}_j + D_{ij} \mathbf{e}_i \times \mathbf{e}_j], \quad (1)$$

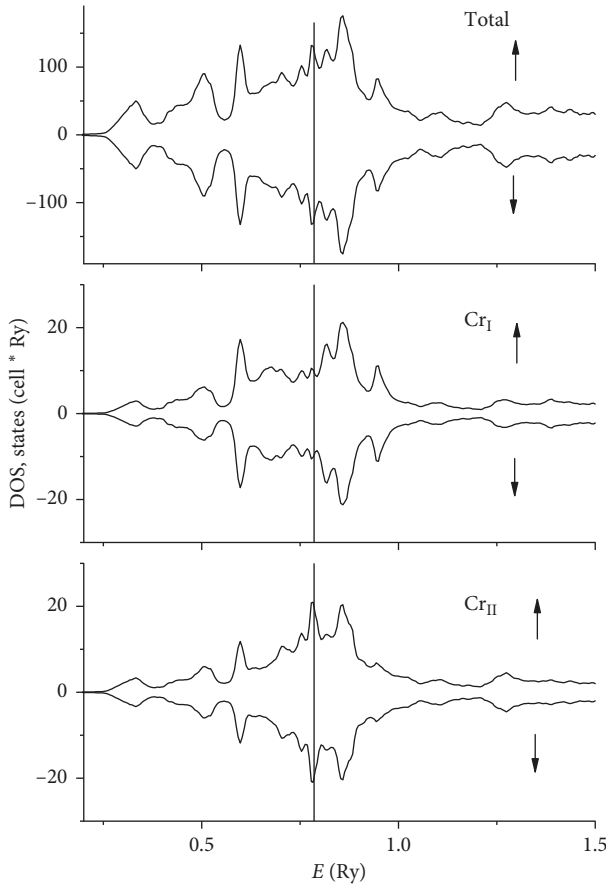
where the direction of the local magnetic moments on the i site is described by unit vectors \mathbf{e}_i . The Hamiltonian contains

TABLE 1: Possible collinear magnetic structures.

No	Atom	Coordinates	FM	FIM	AF1	AF2	AF3	AF4	AF5	AF6	AF7	AF8
1	Cr _I	(0, 0, 0)	+	-	+	+	+	+	+	+	+	+
2	Cr _I	(0.5, 0.5, 0)	+	-	+	+	-	-	-	+	+	-
3	Cr _{II}	(0, 0.5, 0.325)	+	+	-	+	+	-	+	+	-	+
4	Cr _{II}	(0.5, 0, 0.675)	+	+	-	+	+	+	-	-	+	+
5	Cr _I	(0, 0, 1.0)	+	-	-	-	-	-	-	-	-	-
6	Cr _I	(0.5, 0.5, 1.0)	+	-	-	-	+	+	+	-	-	+
7	Cr _{II}	(0, 0.5, 1.675)	+	+	+	-	-	+	-	-	+	-
8	Cr _{II}	(0.5, 0, 1.325)	+	+	+	-	-	-	+	+	-	-

TABLE 2: Calculated parameters of magnetic structures in Cr₂As.

N	Atom	Coordinates	FIM	AF1	AF3	AF4
1	$M(\text{Cr}_I), \mu_B$	(0, 0, 0)	-0.709	0.0	0.937	-0.904
2	$M(\text{Cr}_I), \mu_B$	(0.5, 0.5, 0)	-0.709	0.0	-0.937	0.904
3	$M(\text{Cr}_{II}), \mu_B$	(0, 0.5, 0.325)	1.438	-1.598	1.633	-1.653
4	$M(\text{Cr}_{II}), \mu_B$	(0.5, 0, 0.675)	1.438	-1.598	1.633	1.653
5	$M(\text{Cr}_I), \mu_B$	(0, 0, 1.0)	-0.709	0.0	-0.937	0.904
6	$M(\text{Cr}_I), \mu_B$	(0.5, 0.5, 1.0)	-0.709	0.0	0.937	-0.904
7	$M(\text{Cr}_{II}), \mu_B$	(0, 0.5, 1.675)	1.438	1.598	-1.633	1.653
8	$M(\text{Cr}_{II}), \mu_B$	(0.5, 0, 1.325)	1.438	1.598	-1.633	-1.653
	M_{Total}, μ_B		2.736	0	0	0
	$E_{\text{Total}}, \text{Ry}$		-34847.62952446	-34847.63240435	-34847.63326628	-34847.62949552
	$E - E_{\text{FIM}}, m\text{Ry}$		0	-2.8799	-3.7418	0.0289

FIGURE 3: Density of electronic states for nonmagnetic Cr₂As. Vertical line indicates Fermi energy (E_F), and arrows point to the corresponding spin orientation.

isotropic (J_{ij}^{iso}), symmetric anisotropic (J_{ij}^{sym}) exchange coupling, and Dzyaloshinskii–Moriya interaction (D_{ij}). The Dzyaloshinskii–Moriya interaction $D_{ij} \sim \sum_{\beta \neq 0} J_{0\beta} (\mathbf{r}_{j\beta} \cdot \mathbf{r}_{\beta i})$ is reported in Figure 5. For brevity, these are depicted for the AF3 configuration. The dependence of the exchange couplings from interatomic distance is shown in Figure 6 for the FIM and AF states. Now let us fix the position of an atom of interest as $i = 0$ and consider the exchange parameter with nearby atoms J_{0j} (for convenience, we may omit the zero subscript when it causes no confusion). In the ferrimagnetic phase, the exchange interaction that ensures the bonding of Cr_I and Cr_{II} sublattices is $J_3 = 4.22$ meV in the first coordination sphere and rapidly decreases subsequently (Figure 6). The negative exchange interaction between the nearest Cr_I atoms ($J_1 = -3.52$ meV) ensures their “unusual” orientations in the AF structure (in a nonmagnetic crystal, the Cr_I atoms are symmetrically identical).

Among the exchange integrals that are important for describing the magnetic structure of Cr₂As (Figure 6, Table 3), only J_6 can be considered to be created by the double indirect exchange of Cr_{II}–As–Cr_I atoms. For the other significant exchange integrals, the distance between the cations is smaller or comparable with the distances of the cation-anion [13]. Therefore, it is more appropriate to talk about the mechanism of the classical d-d exchange, which can be either ferromagnetic or antiferromagnetic (ferromagnetic iron and antiferromagnetic manganese or chromium). In other words, the very existence of FM and AFM only phases (lack of intermediate magnetic structure) is due to large value of the d -band electronic filling. This differs substantially from the case of diluted magnetic semiconductors such as Ga_{1-x}Mn_xAs. In the latter case, the

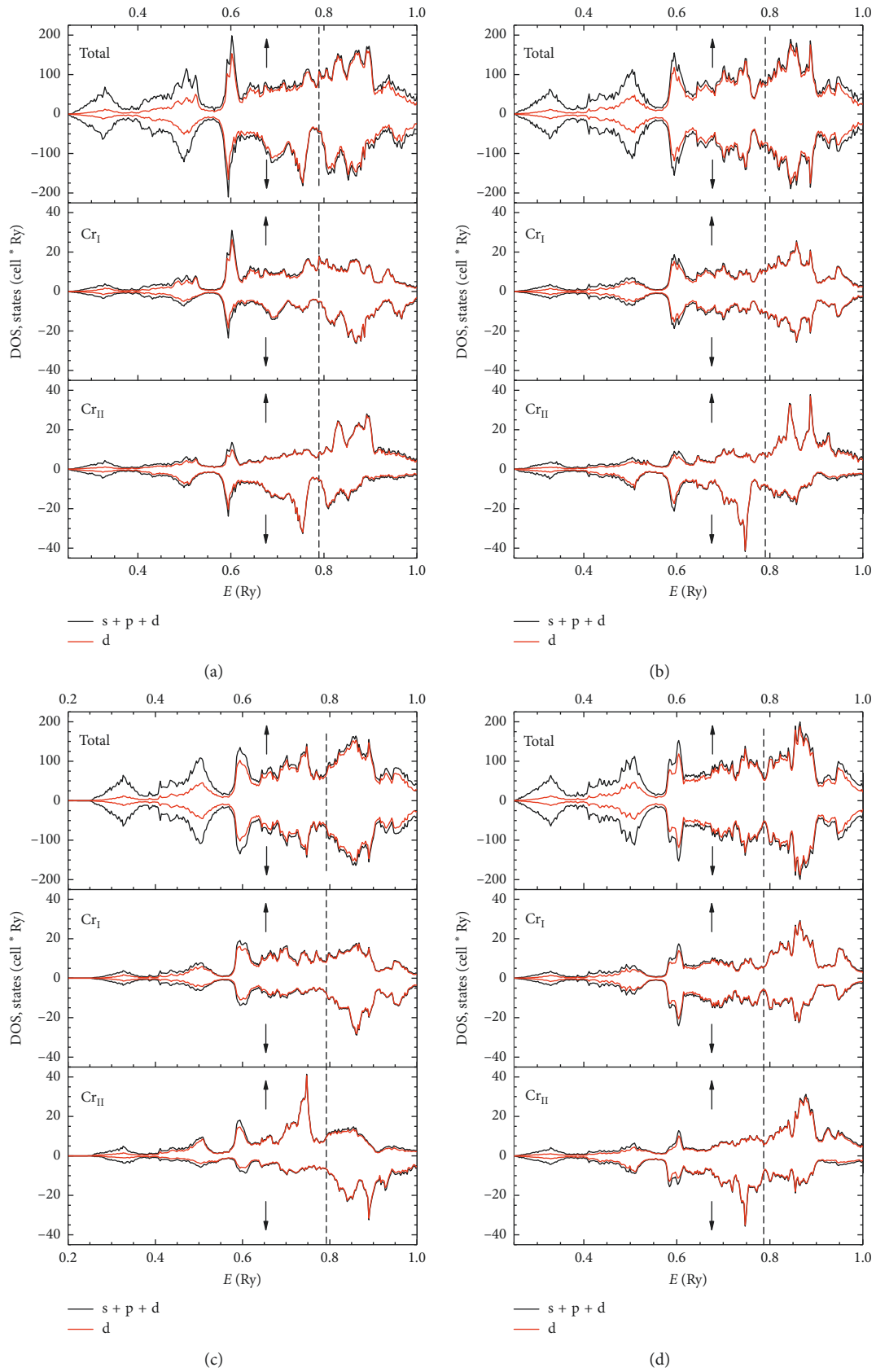


FIGURE 4: Density of electronic states for ferrimagnetic (a) and antiferromagnetic AF1 (b), AF3 (c), AF4, and (d) Cr_2As . Notation follows that of Figure 3.

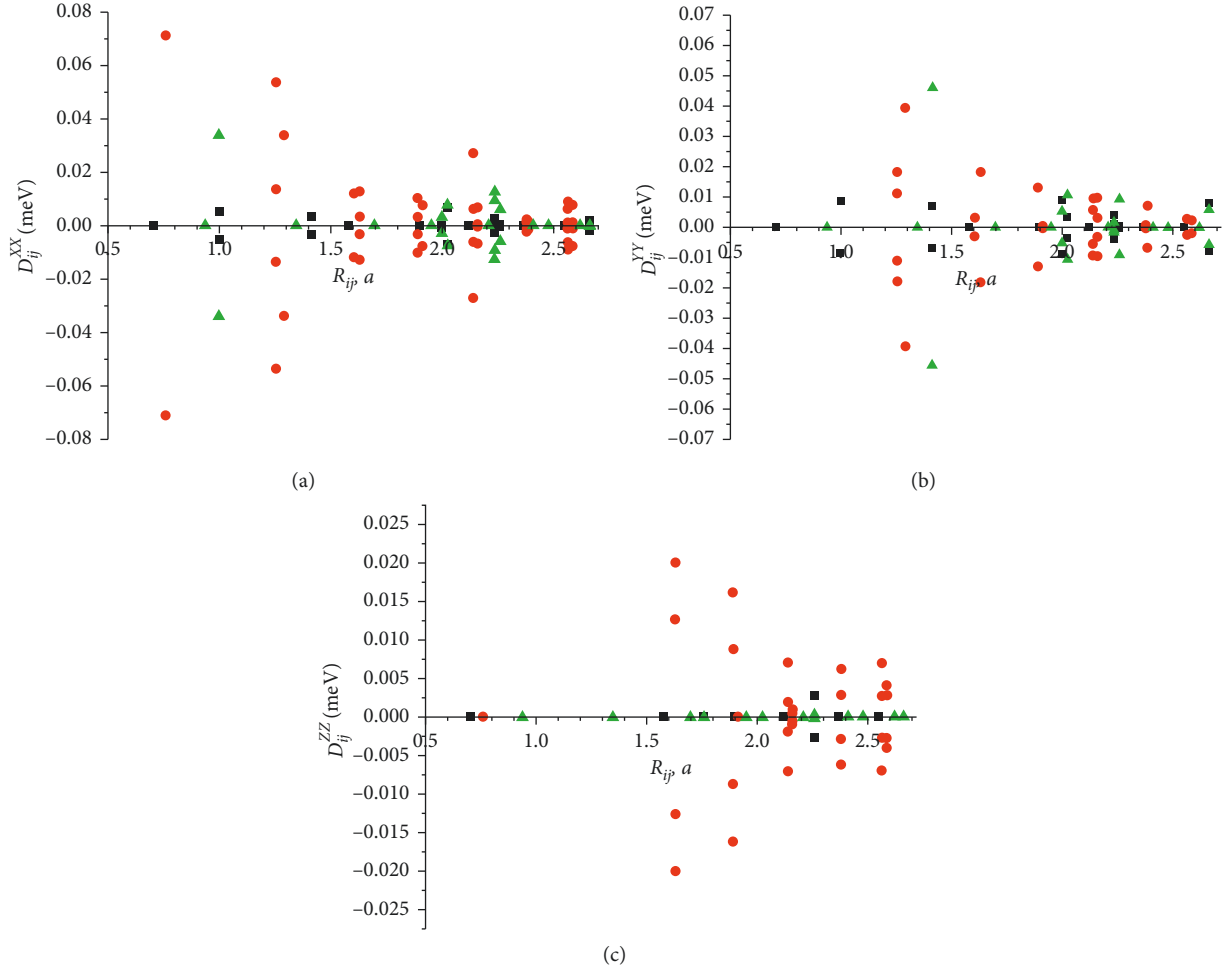


FIGURE 5: Dependence of the diagonal component of Dzyaloshinskii-Moriya interaction D_{ij}^X (a), D_{ij}^Y (b), and D_{ij}^Z (c) in the AF3 structure of Cr_2As from interatomic distance (in lattice units a).

TABLE 3: Dependence of effective interatomic exchange interactions (in meV) from the magnetic structure.

J_{ij}	FIM	AF1	AF3	AF4
J_1	-3.52	0	5.53	5.71
J_2^X	1.81	0	3.79	2.44
J_2^Y	1.81	0	2.98	2.37
J_3^X	4.22	0	4.77	5.36
J_3^Y	4.22	0	-6.36	5.36
J_4^X	8.61	8.47	10.13	12.26
J_4^Y	8.61	8.47	8.66	9.26
J_5	0.66	2.21	1.84	-1.84
J_6	-0.32	5.67	5.18	4.20

interaction of magnetic atoms via nonmagnetic As becomes the dominant mechanism due to the low concentration of manganese atoms [13].

The main topic of interest in Cr_2As is the interrelation between two chromium sublattices, which can be provided only by anisotropic exchange interaction [5, 6]. To estimate its value, the interatomic exchange integrals for the different AF states (Figure 6, Table 3) were calculated. In the case of the AF3 structure, for an arbitrary Cr_I , in one half of the

nearest Cr_{II} atoms, the magnetic moments are parallel, while for the second one, they are antiparallel to the magnetic moment of the chosen atom. The observed difference in the exchange integrals along the X and Y axes $J_3^X(\text{Cr}_I - \text{Cr}_{II}) = 4.77$ meV and $J_3^Y(\text{Cr}_I - \text{Cr}_{II}) = -6.36$ meV confirms the existence of anisotropy of the $\text{Cr}_I - \text{Cr}_{II}$ exchange interaction 6. However, its magnitude is insufficient to ensure simultaneous transition of sublattices to a magnetically ordered state (Figure 2). The anisotropy part of $\text{Cr}_{II} - \text{Cr}_{II}$ exchange interaction is much smaller: $J_4^X(\text{Cr}_{II} - \text{Cr}_{II}) = 10.13$ meV, $J_4^Y(\text{Cr}_{II} - \text{Cr}_{II}) = 8.66$ meV.

We estimate the temperatures of the magnetic ordering of the chromium sublattices by the well-established expression formula: $T_0 = (2/3)J_0$, which is valid for the Heisenberg model with classical spins [12], where $J_0 = \sum_{j \neq 0} J_{0j}$ is the effective exchange interaction of the chosen atom with the entire crystal. The effective ordering temperatures are $T(\text{Cr}_I) = 180$ K and $T(\text{Cr}_{II}) = 382$ K versus experimentally observed $T(\text{Cr}_I) = 175$ K and $T(\text{Cr}_{II}) = 393$ K. The detailed analyses of orientation dependence of magnetic moments and interatomic exchange interaction (Tables 2 and 3) showed that magnetic moment of Cr_I is induced by exchange interaction within the Cr_{II} sublattice.

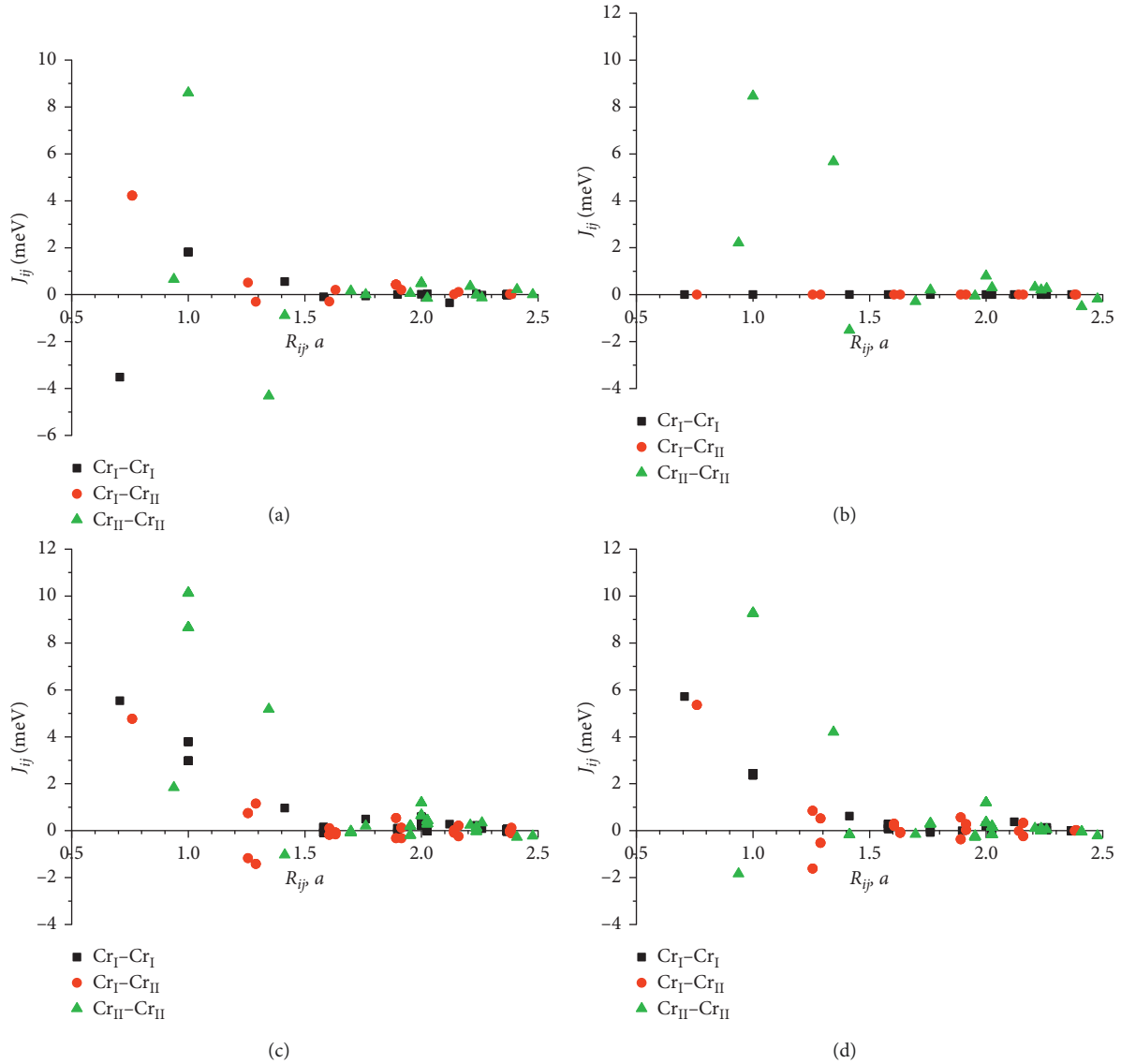


FIGURE 6: Dependence of interatomic exchange interactions in Cr_2As from interatomic distance (in lattice units a) in ferrimagnetic (a) and antiferromagnetic AF1 (b), AF3, (c), AF4, and (d) structures.

As was indicated in [14], estimate of the critical temperature on the basis of mean field approximation is inaccurate and gives too high or too low value, depending on the model used. However for Cr_2As as estimated (experimental results, as shown in Figure 2), the critical temperature for Cr_I and Cr_{II} differs by no more than 3%. Such accuracy justifies the mean field approximations used for calculation of the exchange integrals as compared to the more involved Monte Carlo simulations. The Monte Carlo method improves convergence, provided the underlying code considers the following: (a) the changes in the electronic structure occurring when the magnetic moments of chromium atoms are reoriented; (b) the corresponding changes in exchange integrals; and (c) the effects of percolation in our case are not as important as in diluted magnetic semiconductors [14].

SPR-KKR calculation is based on the LDA. Self-interaction corrections for Kohn–Sham density functional

theory were reported in literature [15, 16]. Their physical meanings, formulations, and applications to the critical temperature of the relevant phase transition have been discussed. In essence, the self-interaction corrections get rid of the self-interaction error, which is the sum of the Coulomb and exchange self-interactions that remain because of the use of an approximate exchange functional. The most frequently used self-interaction correction is the Perdew–Zunger correction. However, this correction leads to instabilities in the electronic state calculations of molecules. To avoid these instabilities, the authors provided several self-interaction corrections on the basis of the characteristic behaviors of self-interacting electrons, which have no two-electron interactions. These include the von Weizscker kinetic energy and long-range (far from the nucleus) asymptotic correction. Applications of self-interaction corrections have shown that the self-interaction error has a

serious effect on the states of core electrons, but it has a smaller than expected effect on valence electrons, as is the case described in our manuscript. The distribution of self-interacting electrons indicates that they are near atomic nuclei rather than in chemical bonds and has a limited effect on the mean field theory. We believe that, at this point, we shall leave those effects to further discussions.

4. Conclusion

In the literature, there is a paper [17] devoted to theoretical analysis by the Berto method [18] of possible magnetic structures and the conditions for their realization in magnets with a tetragonal lattice of the Cu_2Sb type. Fruchart [17] indicates as the crucial parameter for the existence of the AF structure, the large value of the indirect exchange of $\text{Cr}_{\text{II}}\text{-As-Cr}_{\text{II}}$ (J_6 in our notation). However, the applicability of their conclusions to the description of the AF structure in Cr_2As seems doubtful due to the isotropic exchange approximation used [17] to obtain them. Preliminary analysis of magnetic structures by the Berto method [18] showed that, for the realization of the experimentally observed AF structure in Cr_2As , the existence of anisotropy of the exchange interaction ($J^{\uparrow\uparrow}(\text{Cr}_I - \text{Cr}_{\text{II}}) \neq J^{\uparrow\downarrow}(\text{Cr}_I - \text{Cr}_{\text{II}})$) is a necessary condition.

Data Availability

The data used to support the findings of this study are included within this article.

Conflicts of Interest

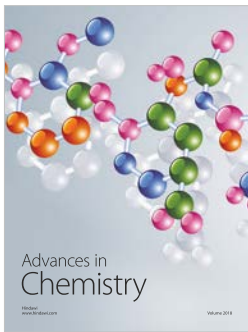
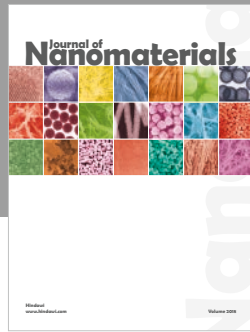
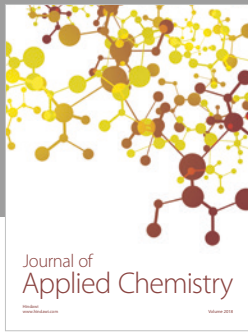
The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

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