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Pressure-induced structural and magnetic phase transition in ferromagnetic CrTe

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Abstract

Self-consistent electronic structure calculations were carried out for ferromagnetic CrTe in NiAs and MnP structure by means of tight-binding linear muffin–tin orbital method. The relative stabilities of the high-pressure phases were studied by means of total energy curves. From the curves it can be clearly seen that NiAs-type CrTe is the stable phase in agreement with the experimental observation. Under pressure, a crystallographic transition from NiAs- to MnP-type occurs around 11.3 GPa. In addition, a magnetic transition from ferromagnetic to non-magnetic state is predicted around 45.3 GPa. The band structure and density of states are plotted for the ferromagnetic (NiAs- and MnP-type structures) and non-magnetic states. The basic ground state properties such as the equilibrium lattice constant, bulk modulus are calculated and compared with the available literature. The possible reason for the structural phase transition is also discussed.

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1. Introduction

Transition metal chalcogen compounds display a wide variety of physical properties depending strongly on the specific stoichiometry. In addition, structural or magnetic phase transitions occur upon varying the temperature, pressure or the composition. For example, the usual phase transition of the second order, which occurs at the Curie

point of the ferromagnet, may become a phase transition of first order at high pressures [1]. Magnetism of NiAs-type transition metal pnictides and chalcogenides have attracted more attention because of a rich variety of magnetic ordering depending on the combination of the metal atom and pnictogen or chalcogen atom. For NiAs-type pnictides such as MnAs, MnSb, CoAs, etc., systematic band calculations are carried out by Motizuki et al. for non-magnetic and magnetic ordered states using a self-consistent augmented plane wave (APW) method [2–4]. Besides, on the basis of the calculated band structure, the anomalous magnetic and elastic behavior observed in

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the paramagnetic phase and the structural phase transformation from NiAs- to MnP-type, are discussed extensively [2,4,5]. For NiAs-type chalcogenides the electronic band calculation of chromium chalcogenides is performed by Dijkstra et al. using augmented spherical wave method, in which the magnetic and transport properties are discussed [6]. NiAs-type CrTe has attracted more attention because among chromium chalcogenides only CrTe becomes a ferromagnet below $T_c = 340$ K, while CrSe and CrS are antiferromagnets [7,8].

The first X-ray study on CrTe was performed by Haraldsen and Neuber [9], in which the existence of two intermediate phases, an α phase with the hexagonal NiAs (B8) structure and a monoclinic β phase are reported. Chevreton et al. [10] performed crystallographic investigations at various compositions. Three ordered NiAs defect derivative phases were characterized: trigonal Cr_2Te_3 with the Cr_2S_3 -type structure [11], monoclinic Cr_3Te_4 with Cr_3S_4 -type structure [11] and monoclinic Cr_7Te_8 with Cr_7Se_8 -type structure [12]. In agreement with Berg [13], the workers showed that stoichiometric CrTe does not exist.

The magnetic properties of CrTe have attracted much interest for its very large magneto-volume effect [14]. The magnetic state of CrTe at high pressure was investigated by Shanditsev et al. [1] using electron spin resonance and by Andron et al. [15] using neutron diffraction. They showed from experiments that ferromagnetism disappeared at pressures above 3.5 GPa at low temperatures. Takagaki et al. [7,16] studied theoretically the pressure effect on the electronic band structure of CrTe using the self-consistent linear augmented plane wave (LAPW) method. Recently, the pressure dependence of the saturation magnetic moment and that of the Curie temperature have been measured by Kanomata et al. [17]. Kawakami et al. [8] using full potential linearized augmented plane wave method (FLAPW) method have reported the ferromagnetic \rightarrow antiferromagnetic transition to be around 40 GPa. Eto et al. [18] by in situ angle-dispersive X-ray diffraction using synchrotron radiation reported a pressure-induced structural transition from NiAs-type to the MnP-type at a pressure around 13 GPa. The value of the bulk modulus at room temperature for the low-pressure

phase is reported to be around 43.8 (5) GPa. So far no literature is available explaining the magnetic \rightarrow non-magnetic transition in CrTe. Hence, efforts are taken in the present work to predict the same by using tight-binding linear muffin tin orbital method (TB-LMTO). In addition, the structural phase transition reported by Eto et al. is also studied by the above method. In this work, the band structure, density of states (DOS) and the bulk modulus are computed and compared with the available literature. The values obtained in the present work are in good agreement with those of others [6,7,18,19]. The rest of the paper is organized as follows. In Section 2, the crystallographic data and the computational details are given. The results are discussed in Section 3. The final section gives the conclusion of this paper.

2. Crystallographic aspects and computational details

The structure of CrTe is the hexagonal NiAs-type [6,20] with the space group $P6_3/mmc$ (194). The Cr and Te atom is positioned at (0,0,0) and $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$, respectively. The cell parameters are $a = 7.5255$ a.u and $c = 11.7410$ a.u [21]. The Cr–Te and Cr–Cr distances are 5.062 and 5.667 a.u, respectively, which compares quite well with the earlier works [6]. The c/a ratio of 1.56 is smaller than the ideal value of 1.63. Six tellurium atoms form a diagonally distorted octahedron around Cr. Six other Cr atoms further surround a Cr atom. The high-pressure phase of CrTe is of orthorhombic (MnP-type) structure. In this structure the Cr atom is positioned at (0.20, 0.005, 0.25) and the Te atom at (–0.07, 0.69, 0.25). The lattice parameters in the orthorhombic structure satisfy the following relations: $a_o = \sqrt{3}a_h$, $b_o = c_h$, and $c_o = a_h$, where subscripts ‘o’ and ‘h’ indicate orthorhombic and hexagonal, respectively. At the transition to the MnP-type structure, each atom shifts slightly from its original position in the NiAs-type structure. The calculated lattice parameter and the nearest neighbor distances are tabulated in Table 1.

To obtain the electronic structure and the basic ground state properties of CrTe, TB-LMTO

Table 1
Calculated ground state properties of CrTe

Property	NiAs (FM)		MnP (FM)	MnP (NM)
	Present	Earlier	Present	Present
Lattice parameter (a.u)	a = 7.2912 c = 11.3742	a = 7.5255 ^a c = 11.7410 ^a	a = 11.7902 b = 10.6194 c = 6.8064	a = 11.0650 b = 9.9662 c = 6.3878
Bulk modulus (GPa)	46.27	43.8 ^b	117.5	267
$N(E_F)$ (States/Ry/FU)	22.95	—	17.12	28.48
γ (mJ/mol K ²)	3.973	—	2.963	4.930
Cr–Cr (a.u)	5.6674	5.8790 ^c	5.4390	5.1044
Cr–Te (a.u)	5.0624	5.2550 ^c	4.9418	4.6378
Magnetic moment (μ_B /formula unit)	2.86	2.60 ^d	1.44	0

^a Ref. [21].

^b Ref. [18].

^c Ref. [6].

^d Ref. [7,16].

method has been used [22,23]. von-Barth and Hedin parameterization scheme has been used for the exchange correlation potential [24] within the local density approximation (LDA). The accuracy of the total energies obtained within the density-functional theory, often even using LDA, is in many cases sufficient to predict which structure at a given pressure has the lowest free energy [25]. Atomic sphere approximation [26] has been used in the present work. In this approximation, the crystal is divided into space filling spheres centered on each of the atomic site. Combined correction terms are also included, which account for the non-spherical shape of the atomic spheres and the truncation of the higher partial waves inside the sphere to minimize the errors in the LMTO method. The Wigner–Seitz sphere is chosen in such a way that the sphere boundary potential is minimum and the charge flow between the atoms is in accordance with the electronegativity criteria, ‘s’ ‘p’ and ‘d’ partial waves are included. The tetrahedron method [27] of the Brillouin Zone (\mathbf{K} space) integration has been used to calculate partial and total DOS. \mathbf{E} and \mathbf{K} convergence is also checked. The basis orbitals used in the calculations are

Cr : 4s¹, 4p⁰, 3d⁵,

Te : 5s², 5p⁴.

3. Results and discussions

3.1. Total energy calculation

In order to study the structural phase stability of CrTe, spin polarized total energy calculations were carried out in a manner similar to our earlier work [28] for ferromagnetic NiAs- and MnP-type structures and non-spin polarized calculation was done for the non-magnetic MnP-type structure in the same manner as that of our previous works [29,30] by reducing the volume from 1.05 V_0 to 0.6 V_0 , where ‘ V_0 ’ is the experimental equilibrium volume. The experimental work of Eto et al. [18] report a crystallographic transition from NiAs structure to MnP structure. Kawakami et al. [8] has reported a pressure-induced magnetic transition from ferromagnetic to antiferromagnetic state in CrTe. In the present work, efforts were taken to determine the transition to the non-magnetic state in addition to the structural phase transition.

The calculated total energies are fitted to the Birch equation of state [31] to obtain the pressure volume relation. The graph connecting the pressure and relative volume in the ferromagnetic NiAs- and MnP-type and the non-magnetic MnP type of CrTe is shown in Fig. 1. The pressure is obtained by taking the volume derivative of the total energy. The Bulk modulus is also calculated

from the $P-V$ relation.

$$B = -V dP/dV. \quad (1)$$

The theoretically calculated lattice constant and the bulk modulus in the magnetic and non-magnetic phase of CrTe are tabulated in Table 1 and are compared with the available experimental results [18,21].

3.2. Structural phase transition

The structural phase stability is determined by calculating Gibb's free energy for the NiAs- and MnP-type ferromagnetic CrTe, which is

$$G = E_{\text{tot}} + PV - TS. \quad (2)$$

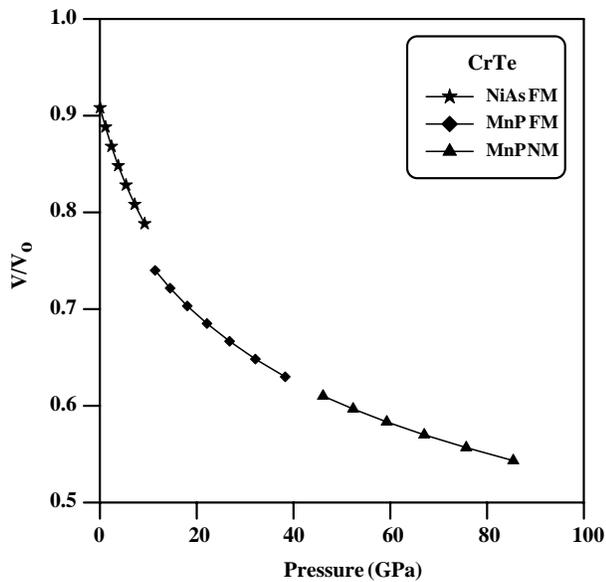


Fig. 1. Calculated pressure volume relation in the NiAs and MnP (FM and NM)-type structures of CrTe.

Since the theoretical calculations are performed at 0 K, Gibbs free energy becomes equal to the enthalpy (H)

$$H = E_{\text{tot}} + PV. \quad (3)$$

At a given pressure, a stable structure is one for which enthalpy has its lowest value and the transition pressures are calculated at which enthalpies for the two phases are equal. The transition pressure from NiAs to MnP structure and the volume collapse are given in Table 2 and are compared with the available literature [18]. The graph connecting the total energy and the relative volume in the NiAs and MnP (magnetic)-type structures is given in Fig. 2. From the graph, it can be clearly seen that NiAs-type ferromagnetic

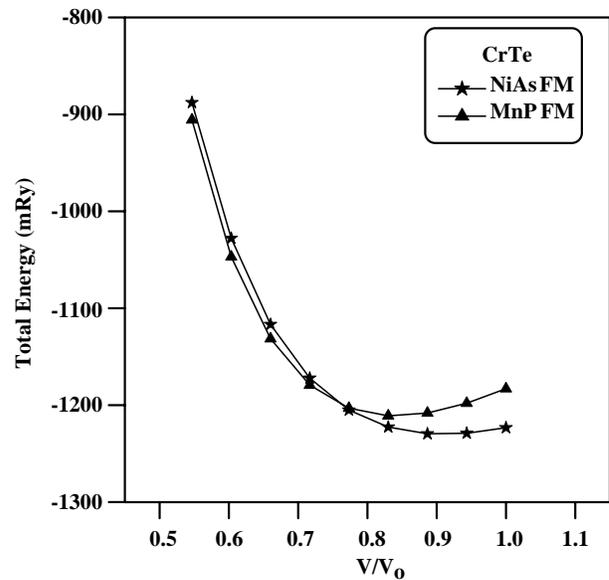


Fig. 2. Calculated total energy ($-15677.00+$) Ry vs. relative volume in the ferromagnetic phase of CrTe.

Table 2
Calculated transition pressure and volume collapse of CrTe

CrTe	Transition Pressure (GPa)		Volume collapse (%)	
	Present	Experimental	Present	Experimental
Structural NiAs \rightarrow MnP	11.3	13 ^a	4	1.2 ^a
Magnetic MnP (FM) \rightarrow MnP (NM)	45.3	—	—	—

^a Ref. [18].

CrTe is the most stable phase. The magnetic moment per formula unit of CrTe in the stable phase is around $2.86 \mu_B$. The magnetic moment decreases as the lattice constant decreases due to the applied pressure. At a pressure of about 11.3 GPa, there is a structural phase

transition from the NiAs-type structure to the MnP-type structure, which is in fairly good agreement with the value of 13–14 GPa reported by Eto et al. [18].

In MnAs, a 3d transition metal pnictide, Menyuk et al. [32] has observed that the structural phase transition from NiAs- to MnP-type is accompanied by the ferromagnetic to antiferromagnetic transition at about 0.4 GPa and 200 K. Hence, one may think of a magnetic transition in CrTe also. However, the mechanism of phase transition in CrTe would be different from that of MnAs, because the transition pressures for the magnetic and structural transition in CrTe differ by more than 20 GPa. In CrTe, the ferromagnetic to antiferromagnetic transition is reported to be around 40 GPa [8]. In the present work, total energies were computed for the non-magnetic state of MnP-type CrTe, in order to study the magnetic transition from ferromagnetic MnP-type CrTe to the non-magnetic state. Up to the crystallographic transition there is no magnetic transition observed.

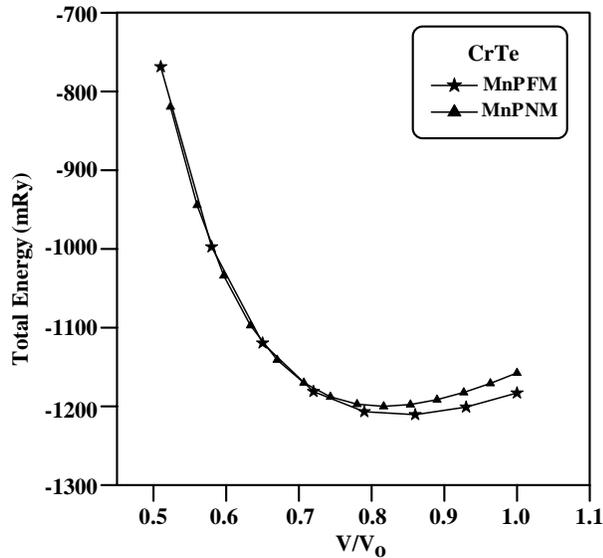


Fig. 3. Calculated total energy ($-15677.00+$) Ry vs. relative volume in the MnP- type (FM and NM) phase of CrTe.

3.3. Magnetic phase transition

The magnetic moment in the MnP phase is around $1.44 \mu_B$. The moment decreases for

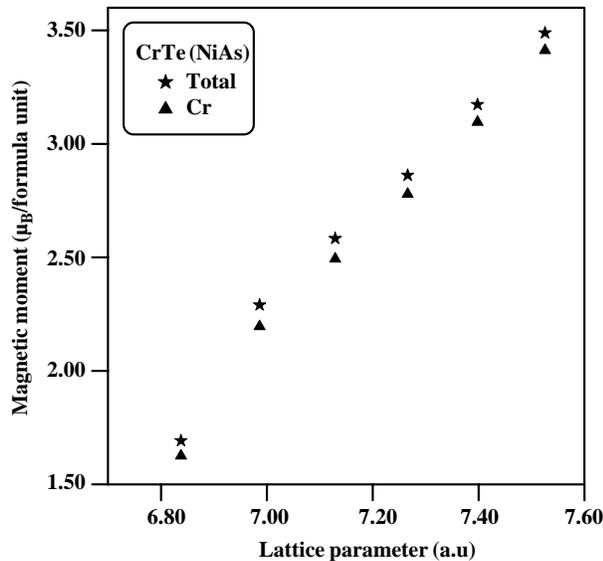


Fig. 4. Pressure dependence of magnetic moment in the NiAs-type CrTe.

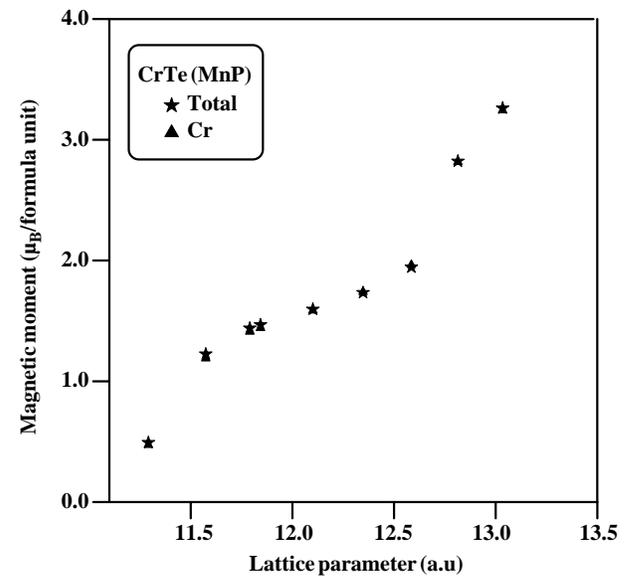


Fig. 5. Pressure dependence of magnetic moment in the MnP-type CrTe.

increasing pressures and almost vanishes at $a = 11.0650$ a.u. Hence, one can expect a phase transition to the non-magnetic phase. This transition is predicted to be around 45.3 GPa. The graph connecting the total energy and the relative volume in both the magnetic and non-magnetic phase of MnP-type CrTe is shown in Fig. 3. From the graph it can be clearly seen that magnetic MnP state is stable when compared to the NM state and at high pressure there is a transition to the non-

magnetic state. The calculated transition pressure for the structural and magnetic phase transition and the corresponding volume collapse is reported in Table 2.

3.4. Pressure effect on the magnetic moment of ferromagnetic NiAs- and MnP-type CrTe

The pressure dependence of the calculated total magnetic moment of the ferromagnetic state of

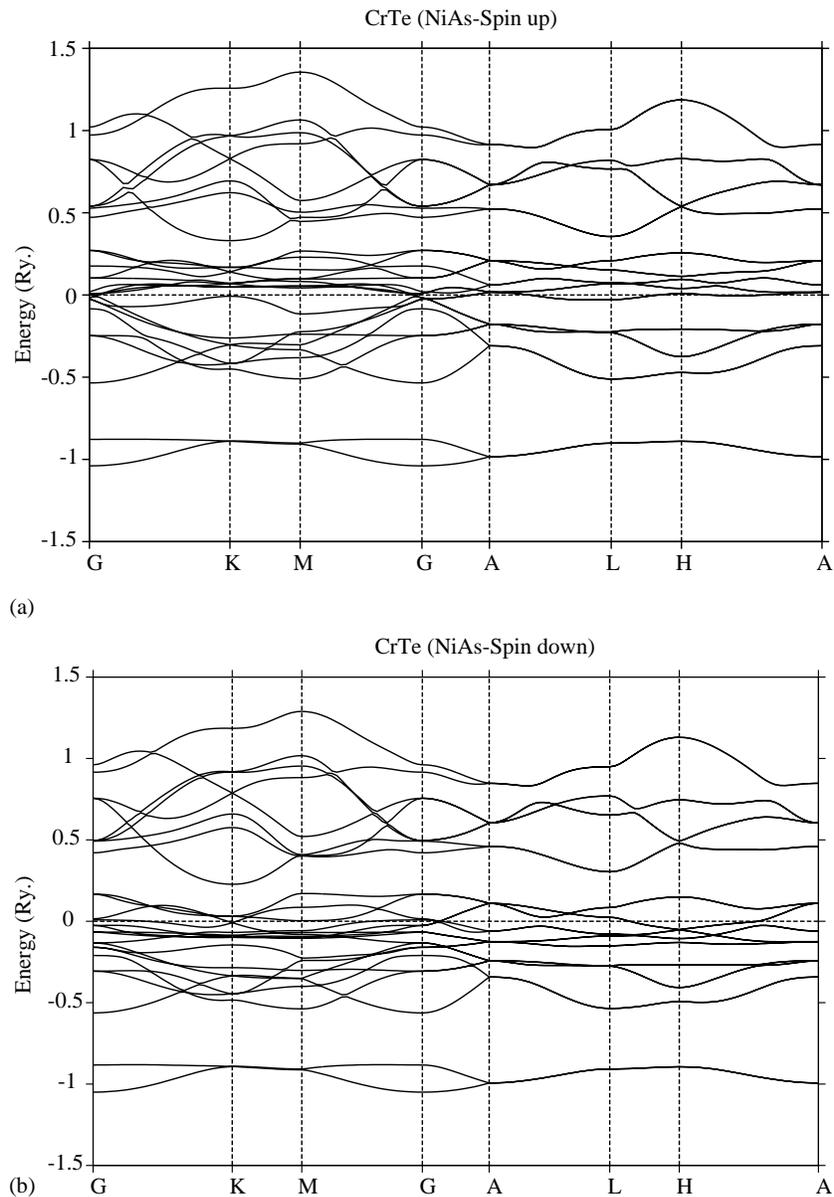


Fig. 6. Band structure in the NiAs phase of CrTe (a) spin up (b) spin down.

NiAs- and MnP-type CrTe are shown in Figs. 4 and 5 respectively. In both the structures, the magnetic moment arises mainly from the Cr-site. In the ferromagnetic ordering, the hybridization of the transition-metal 3d states with the anion ‘p’ states causes a positive magnetic polarization of the anion [19]. In CrTe, the metal ‘3d’ state lies above the chalcogen ‘p’ like states. In this, case the hybridization between Cr ‘3d’ like states with the

Te ‘5p’ like states pushes the p (spin up) states to lower energy than the p (spin down) states resulting in the positive polarization of the chalcogen atom.

3.5. Band structure and density of states

The band structure along the symmetry directions for ferromagnetic CrTe (NiAs and

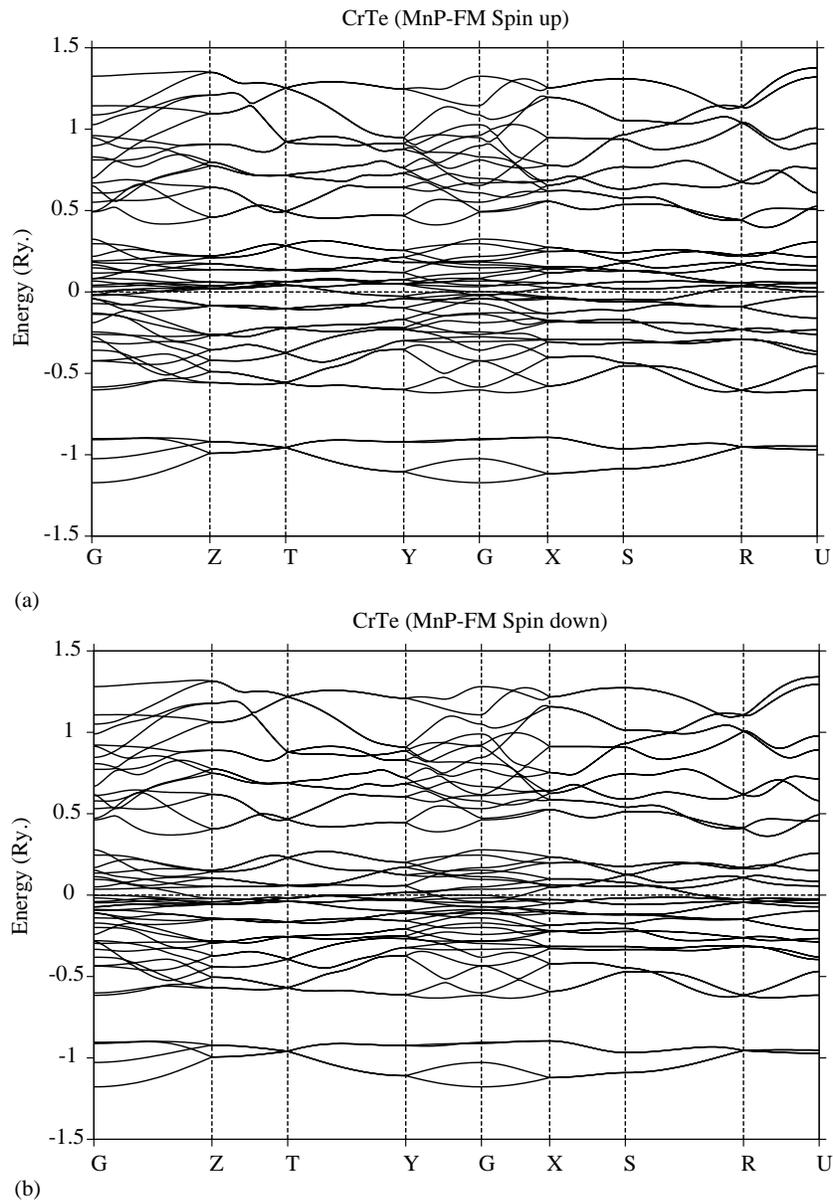


Fig. 7. Band structure in the MnP (FM) phase of CrTe (a) spin up (b) spin down.

MnP)-type structures (both spin up and spin down) and non-magnetic CrTe (MnP) are shown in Figs. 6–8, respectively.

In the NiAs-type CrTe, the bands which are lying around -1 Ry are mainly due to the Te ‘s’ like states which are well separated from the bands that are taking part in conduction. The bands lying above this are mainly contributed by Cr ‘s’ like

states. The bands lying immediately above this are mainly due to Cr ‘p’ like states. The hybridized bands of Te ‘p’ like and Cr ‘d’ like states lies close to the Fermi level. The band structure profiles of spin up and spin down NiAs-type CrTe are almost same. The slight difference which can be seen at the G point is that the hybridized bands of Te ‘5p’ like states and Cr ‘3d’ like states shifts towards the

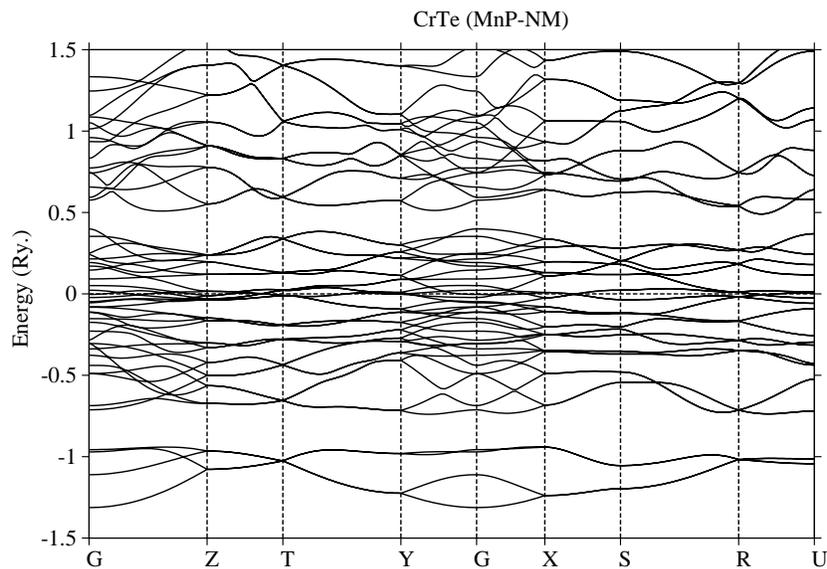


Fig. 8. Band structure in the MnP (NM) phase of CrTe.

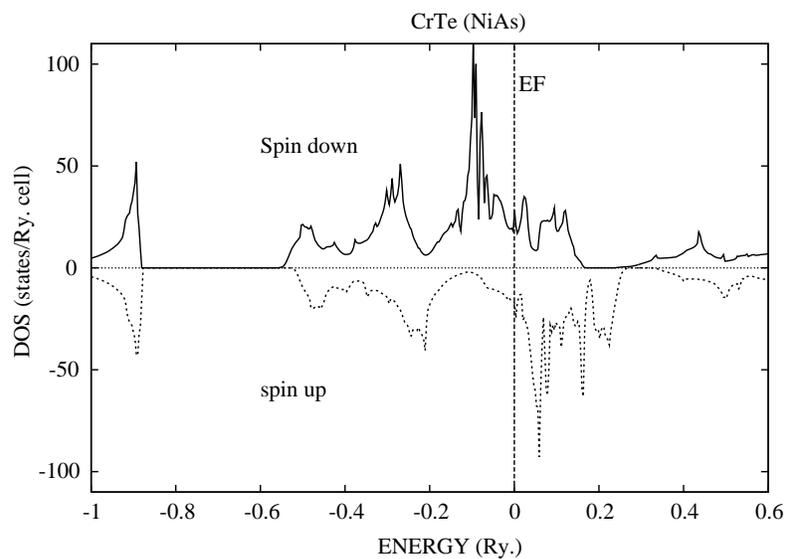


Fig. 9. Density of states in the NiAs phase of CrTe.

lower energy in spin up and lies above the Fermi level which is not the case in spin down. This may be one of the reasons why there is small magnetic moment induced in the Te ‘p’ sites.

In the MnP (FM)-type structure, the lowest lying bands are contributed by the chalcogen ‘s’ like states. As in the NiAs-type structure there is a hybridization between Cr ‘d’ like states and Te ‘p’

like states. The only difference between spin up and spin down band structures is that, along the $Z-T$ direction, the hybridized bands of Te ‘p’ and Cr ‘d’ like states shifts towards the lower energy side and lies above E_F in the spin up state similar to the NiAs-type structure.

In the MnP (NM)-type structure, the lowest band is the Te ‘s’ like states. The hybridized bands

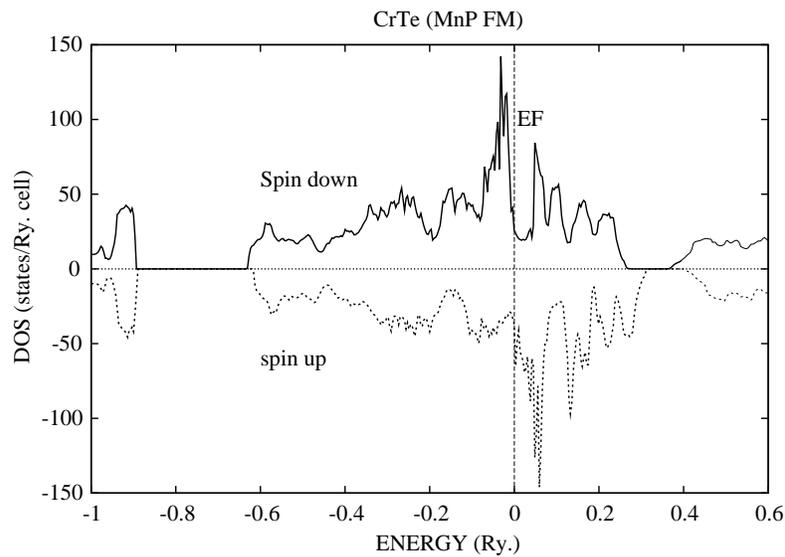


Fig. 10. Density of states in the MnP (FM) phase of CrTe.

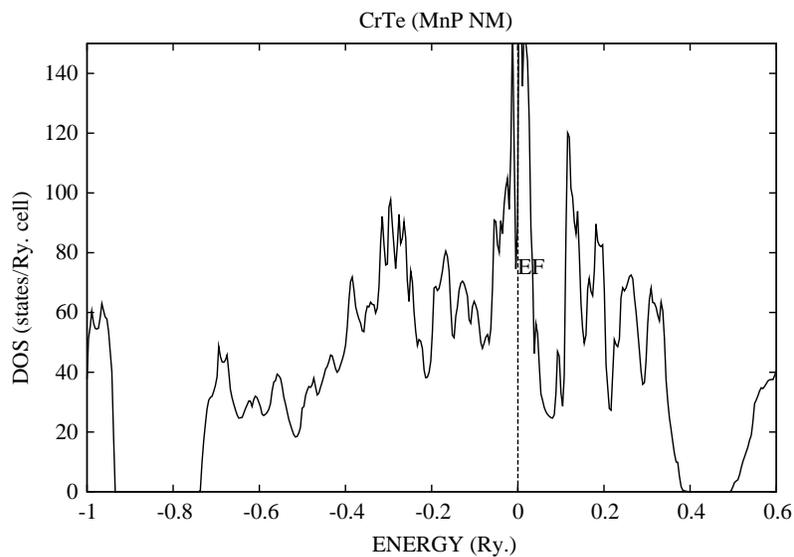


Fig. 11. Density of states in the MnP (NM) phase of CrTe.

Table 3
Partial number of electrons as a function of pressure in NiAs-type CrTe

V/V_0	Cr			Te			
	s	p	d	s	p	d	f
1.00	0.484	0.675	4.738	1.776	3.776	0.391	0.159
0.95	0.481	0.685	4.773	1.750	3.711	0.429	0.171
0.90	0.477	0.695	4.808	1.724	3.644	0.468	0.184
0.85	0.476	0.702	4.843	1.700	3.571	0.510	0.198
0.80	0.475	0.709	4.881	1.674	3.495	0.551	0.216
0.75	0.471	0.710	4.937	1.645	3.402	0.596	0.237
0.70	0.462	0.711	5.001	1.616	3.317	0.627	0.265
0.65	0.460	0.721	5.037	1.586	3.222	0.658	0.295

of Cr ‘d’ like and Te ‘p’ like states lies exactly on E_F unlike the spin up and spin down FM states wherein the hybridized bands lie above and below E_F , respectively.

The DOS histogram of spin up and spin down states of ferromagnetic NiAs- and MnP-type structures and non-magnetic MnP-type structures are given in Figs. 9–11, respectively. The DOS histogram of NiAs-type ferromagnetic CrTe compares well with the earlier work [7]. The peak present around -1 Ry in both NiAs and MnP (FM)-type structure is mainly due to Te ‘s’ like states. The peaks present close to the E_F are due to the hybridized Cr ‘3d’ and Te ‘5p’ like states. As one goes from NiAs (FM) \rightarrow MnP (FM) \rightarrow MnP (NM), the peaks gradually shifts towards E_F and lies exactly on E_F in the NM states. From the calculated DOS at the Fermi energy the electronic specific heat coefficient is calculated using the expression, $\gamma = \pi^2/3k_B^2 N(E_F)$. The calculated values are tabulated in Table 1.

The partial number of electrons is given in Table 3. From the table it can be seen that there is a transfer of electrons from the chalcogen ‘s’ and ‘p’ like states to the Cr ‘d’ like states, which may be one of the reasons for the observed structural phase transformation under pressure.

4. Conclusions

The theoretical study on the ferromagnetic CrTe concludes the following features:

- (1) Ferromagnetic CrTe, which crystallize in NiAs-type structure has a magnetic moment of $2.7 \mu_B$, which mainly arises from the ‘Cr’ site.
- (2) Pressure-induced structural phase transition from NiAs-type occurs around 11.3 GPa which compares well with the reported value of 13 GPa [18].
- (3) The continuous transfer of electrons from the chalcogen ‘s’ and ‘p’ like states to the Cr ‘d’ like state as seen from Table 3 may be the possible reason for the above-mentioned transition.
- (4) In addition, a magnetic phase transition from ferromagnetic to non-magnetic state is predicted to be around 45.3 GPa.
- (5) The major contribution to the DOS is from the Cr ‘d’ like states as can be seen from the DOS histogram.
- (6) The basic ground state properties such as equilibrium cell parameter, bulk modulus, electronic specific heat coefficient are calculated and are in good agreement with the earlier literature.

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