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Lattice Dynamics of superionic crystal $Mn_xCd_{1-x}F_2$

Sudhakar Gupta* and U.P. Singh

**Deptt. Of Physics, T.D. College, Jaunpur, (U.P.), INDIA*
Email – sudhakar.gupta@yahoo.co.in

Abstract

In the present paper Bond Bending Rigid Model (BBRIM) is used to study the lattice dynamical properties of the mixed superionic crystal $Mn_xCd_{1-x}F_2$. Phonon disperson relations, phonon density of states and specific heat at constant volume have been calculated. The nature of the graph satisfies the well known relation $C_v = 3$ R at higher temperatures. Due to unavailability of the experimental results of specific heat for $Mn_xCd_{1-x}F_2$, We can not compare our predicted theoretical results with the experiment.

Keywords: BBRIM, Phonon dispersion relation, Phonon density of states

Introduction

CdF_2 doped with Mn were the subject of various studies[Barinsso (1984), Ciepielewski (1985), Kowalski (1987), Majewski (1985), Suchocki (1985)]. The nature of these interesting crystals due to the magnetic properties of manganese, still appears to be not fully recognized. Mixed crystal $Mn_xCd_{1-x}F_2$ is derived from two compounds with markedly different physical properties. The CdF_2 crystals are diamagnetic and have a fluoride structure, whereas the MnF_2 crystals are antiferromagnetic (below 67K) and have rutile (TiO_2) structure.

Mixed crystal $Mn_xCd_{1-x}F_2$ for $x<0.26$ crystal lies in the fluorite structure with cat ion sites randomly substituted by Cd or Mn ions[Andrzej (1988)]. The primitive rhombohedric cell consists of two F anions and a Mn or Cd ion in the cation site. Andrzej et al.(1988) have proposed a theoretical model to describe the behaviour of the main IR and Raman active mode along with the prominent 'impurity' one in the mixed $Mn_xCd_{1-x}F_2$ Crystal and they described the impurity mode as one of the most which is originated from a gap or local mode of an impurity in the pure parental crystal. But in the present analysis, we have proposed only one set of long wavelength optical phonon frequencies in the entire composition range, assuming MnF_2 crystal as a fluorite structure.

Table (1): Input data of $Mn_xCd_{1-x}F_2$

		MnF_2	CdF_2
Elastic constant (10^{11} dynes cm^{-2})	C_{11}	10.3[a]	18.27[c]
	C_{12}	8.16[a]	6.674[c]
	C_{44}	3.0[a]	2.175[c]
Zone Centre frequencies (cm^{-1})	ω_{LO}	460.98[b]	412[d]
	ω_{TO}	291.45[b]	215[d]
	ω_R	335.42[b]	320[d]
Lattice constant (10^{-8}cm)	a	4.873[a]	5.388[e]
Mass (10^{-24}gm)	M_{cation}	91.75	187.708
	$M_{fluorine}$	31.73	31.73

References
a [Manasreh(1985)]
b [Andrezej (1988)]
c [Singh (1974)]
d [Kosacki (1986)]
e[Cran (1974)]

Table (2): Model Parameters

		MnF_2	CdF_2
Force constants (10^4 dynes cm^{-1})	A_1	8.916	7.337
	A_2	0.174	0.903
	$A_3=A_4$	0.086	0.079
	B_1	0.008	-0.405
	B_2	-0.368	-0.628
	K_1	0.603	1.4516
	K_2	-0.570	-3.354
Effective charge	Z_{eff}	1.304	1.677

The input data for fixing the force constants A_1, A_2, ($A_3=A_4$), B_1, B_2, K_1, K_2 and Z_{eff} are given in table 1.The computed short range force constants and the effective charge are presented in table 2 for the end members .The force constants(α), lattice constants(a and c), masses(m) and effective charges(Z_{eff}) for $Mn_xCd_{1-x}F_2$ is determined by the fallowing equations-

$\alpha (Mn_xCd_{1-x}F_2) = x.\ \alpha (Mn_xCd_{1-x}F_2) + (1-x)\ \alpha (Mn_xCd_{1-x}F_2)$ (1.1)

$a (Mn_xCd_{1-x}F_2) = x.\ a (Mn_xCd_{1-x}F_2) + (1-x)\ a (Mn_xCd_{1-x}F_2)$ (1.2)

$m (Mn_xCd_{1-x}F_2) = x.\ m (Mn_xCd_{1-x}F_2) + (1-x)\ m (Mn_xCd_{1-x}F_2)$ (1.3)

$Z_{eff} (Mn_xCd_{1-x}F_2) = x.\ Z_{eff} (Mn_xCd_{1-x}F_2) + (1-x)\ Z_{eff} (Mn_xCd_{1-x}F_2)$ (1.4)

One-Mode Behavior

To investigate the one-mode behavior in the mixed system $Mn_xCd_{1-x}F_2$ for $x < 0.26$, the force constants and affective charge of the end-members MnF_2 and CdF_2 have been evaluated by the equations (1.1) and (1.4). The variation of zone center frequency of the mixed system with composition is presented in Fig. [1]. The experimental results of Andrej et al.(1988) for $x < 0.26$ is also marked. From the figure it is clear that the predicted theoretical frequencies are in very good agreement with the experimental data [Andrzej(1988)]. One should note that the agreement is good only in the region where CdF_2 is dominant with a fluorite structure.

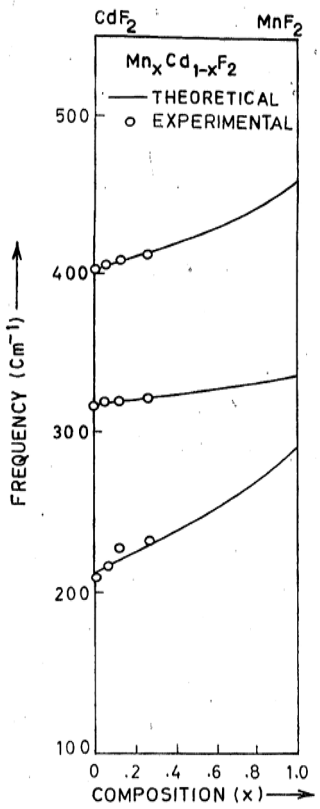

Figure 1

The Dispersion Relations

The phonon dispersion curves of the mixed system $Mn_xCd_{1-x}F_2$ at $x = 0.2$ have been shown in Fig. [2]. The model is giving three imaginary phonon frequencies along [q00] direction as one approaches to zone boundary from zone centre along with one imaginary frequency along [qq0] direction. These imaginary frequencies are not shown in the Fig. [2]. The occurrence of imaginary frequencies may be due to our consideration of MnF_2 as fluoride structure. The Raman and both the IR modes agree very well with the experimental measurements.

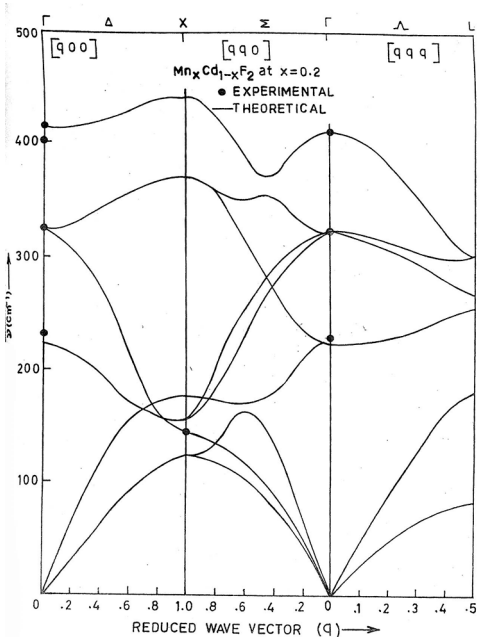

Figure 2

Phonon Density of States

The phonon density of the states the mixed system $Mn_xCd_{1-x}F_2$ at x = 0.2 has been calculated by solving the secular determinant at 48 non-equivalent points. The obtained frequencies are divided into the intervals of $\Delta\nu$ = 20 cm^{-1}. The frequency distribution of mixed system is plotted in the Fig. [3]. The peaks below 200cm^{-1} are due to acoustical phonon frequencies while those at higher than 200cm^{-1} are due to optical frequencies of the mixed crystal.

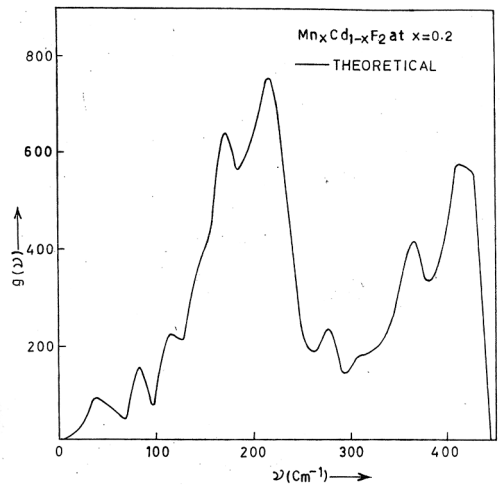

Figure 3

Specific Heat

The variation of specific heat at constant volume with temperature is shown in Fig. [4] for the mixed system $Mn_xCd_{1-x}F_2$ using Blackman's sampling technique[Blackman (1937)]. The model is used to derive the relation of specific heat with temperature. As was obvious from the density of states curve, nature of the graph satisfies the well known relation Cv=3R at higher temperatures. Due to unavailability of the experimental results of specific heat $Mn_xCd_{1-x}F_2$, . We can not compare our calculated theoretical results with the experiment.

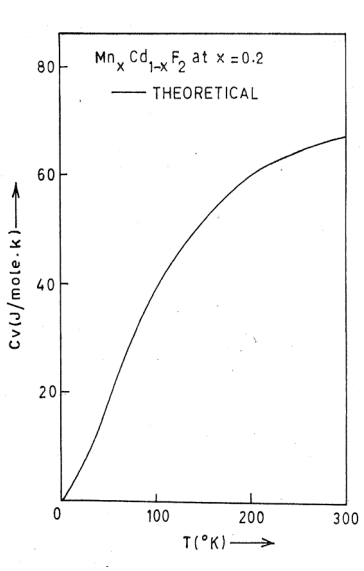

Figure 4

Conclusion

On the basis of present study we can conclude that $Mn_xCd_{1-x}F_2$ are characterized by one mode behavior of the infra red reflectivity spectrum. The composition dependence of cation-cation interaction coefficient determined for $Mn_xCd_{1-x}F_2$ crystal. The Mn-F interaction is weak in compression to F-F interaction. The result of the investigation also show that the disordering of cat ion sub lattice which takes place as crystal changes from MnF_2 to CdF_2, enhances its super ionic properties.

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