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BRIEF COMMUNICATION

Effect of Angular Forces on the Phonons in Defect Chalcopyrite $CdGa_2S_4$

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The phonons in defect chalcopyrite $CdGa_2S_4$ are investigated without and with deLauney-type angular forces. It has been observed that angular forces play a very important role in determining the phonons in defect chalcopyrite structure. The agreement between theory and experiment is good when the angular force contribution is incorporated. The physical significance of the importance of angular force is discussed. © 1994 Academic Press, Inc.

$CdGa_2S_4$ is a tetragonal crystal ($a = b = 5.549$ Å, $c = 10.162$ Å) with one formula unit per unit cell which is characterized by a tetrahedral atomic configuration in which two sites of the cationic lattice of a chalcopyrite structure are free, giving a defect chalcopyrite or a thiogallate structure. These semiconducting ternary compounds have potential applications in photoconduction, nonlinear optics, laser action, etc. (1). The technological applications and the presence of the "defects" in the structure have generated interest in the study of order-disorder phenomena, band structure, and lattice dynamics. Earlier lattice dynamical studies (2–7) have met with limited success. One of the reasons is the presence of the vacancies which soften the interaction between neighboring units and therefore suggest that angular forces may be an important part of the dynamical matrix contribution. Therefore, in this work, the zone center phonons in the case of $CdGa_2S_4$ are investigated, incorporating the deLauney-type angular force (8).

At the center of the Brillouin zone, the vibrational spectrum is given by

$$3A + 6B + 6E.$$

All the optical modes are Raman active, whereas B and E (doubly degenerate) modes are infrared active also. One B and one E mode are acoustic modes. The crystallographic cell is shown in Fig. 1. In order to obtain the zone center phonons, the interatomic interactions as given in Table 1 are considered. Initially, the phonons were calculated by considering only the central forces for all interatomic neighbors. The result was not satisfactory, as is evident from Table 2. As mentioned earlier, in these structures, the full valence requirement creates a number of regularly arranged stoichiometric vacancies in the host lattice which indicate that the angular forces may play a vital role. Hence, angular forces among sulpher ions were considered and, as is obvious from Table 2, each one is

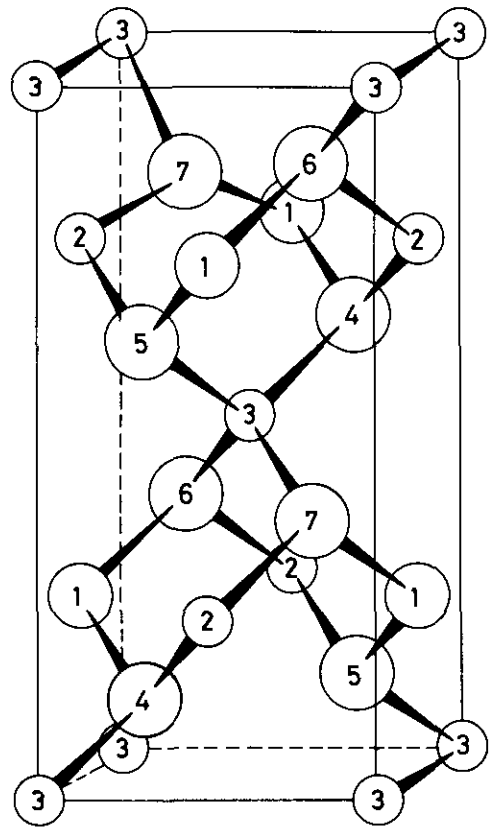

FIG. 1. Structure of defect chalcopyrite AB_2X_4 (1 = A atom; 2, 3 = B atom; 4, 5, 6, 7 = X atom).

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TABLE 1
Interatomic Interactions in $CdGa_2S_4$

Atoms involved	Force constant	Nature	Value (in N/m)
Ga(2)–S	α_1	Central	60.0
Ga(3)–S	α_2	Central	90.0
Cd(1)–S	α_3	Central	155.0
Cd(1)–Ga(3)	α_4	Central	30.0
Cd(2)–Ga(3)	α_5	Central	50.0
S(5), S(4)–S(6), S(7)	α_6	Central	35.0
	α_6'	Angular	See Table 2
Cd(1)–Ga(2)	α_7	Central	10.0
S(4)–S(5) S(6)–S(7)	α_8	Central	20.0
	α_8'	Angular	See Table 2

TABLE 2
Effect of Angular Forces (in N/m) on the Zone Center Phonons (in cm^{-1}) in $CdGa_2S_4$

Mode	$\alpha_6' = 0$ $\alpha_8' = 0$	$\alpha_6' = 0$ $\alpha_8' = -10.0$	$\alpha_6' = -10.0$ $\alpha_8' = 0$	$\alpha_6' = -10.0$ $\alpha_8' = -10.0$	Experimental (9) for A mode and (4) for B and E mode
A	448	442	400	391	393
	387	364	341	315	312
	329	298	275	239	219
B	426	405	396	376	372
	368	347	338	321	323
	263	261	260	256	254
	226	211	203	176	162
	150	143	139	127	142
E	421	412	381	366	362
	352	327	317	305	324
	257	240	245	230	240
	207	206	170	153	135
	167	138	139	91	84

quite significant in explaining the phonons in these defect chalcopyrite structures. The agreement obtained between theory and experiment supports the proposition that because of vacancies in the cationic sublattice of the chalcopyrite structure, the bonds among the various ions become angled. This physically justifies the inclusion of angular forces in the defect chalcopyrite structures.

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