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Lattice Dynamics of Oxide-Spinel $ZnCr_2O_4$

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The short-range force model has been applied to study the zone-center phonon frequencies of oxide-spinel $ZnCr_2O_4$. A comparative study of interatomic forces is also made between oxide-spinel $ZnCr_2O_4$ and chromium sulfide/selenide spinels. Our short-range model provides fair agreement with the available experimental results. © 1993 Academic Press, Inc.

In the past, various studies of the electrical, magnetic, and vibrational properties of normal spinels have been reported, and have attracted considerable experimental and theoretical interest (*1, 2*). $ZnCr_2O_4$ is a normal spinel, with space group $Fd3m$ (O_h). The primitive rhombohedral unit cell contains two formula units, with the oxygen ions forming a cubic close-packed structure. The Cr and Zn ions are octahedrally and tetrahedrally coordinated, respectively, by the oxygen ions. Group theoretical treatment of the optical zone-center ($k = 0$) phonon modes yields (*3*)

$$\Gamma = A_{1g} + E_g + F_{1g} + 3F_{2g} + 2A_{2u} + 2E_u + 4F_{1u} + 2F_{2u}.$$

Recently, Himmrich and Lutz (*3*) performed normal coordinate analyses and lattice dynamical calculations for the spinel-type $ZnCr_2O_4$ with the short-range (SRM), rigid-ion (RIM), and polarizable-ion (PIM) models. They have found that, contrary to spinel-type chromium sulfides (*4*), the contribution of coulomb forces (LRFC) is important for most modes of $ZnCr_2O_4$ and therefore they concluded that the short-range model is too crude to describe the potential energy of the relatively ionic compound $ZnCr_2O_4$. Both rigid-ion and polarizable-ion models are equally appropriate to the lattice dynamics of $ZnCr_2O_4$, and finally they decided that the results obtained by the PIM were the most reliable. But, experimentally it is found that of four, only two of the F_{1u} modes split up into LO and TO branches, differing in magnitudes by not more than 12% for $ZnCr_2O_4$ (*5*) and 7–8% for chromium sulfide spinels (*4*); therefore, the consideration of long-range coulomb forces is not important enough to reduce the E_u (2) and F_{2u} (2) frequencies to a very low value (*3*). In the present investigation, a short-range force model on the lines of de Launey (*6*) has been applied to study the zone-center phonons of oxide-spinel $ZnCr_2O_4$. The zone-center phonon frequencies thus calculated are found to be in agreement with the available experimental results. The comparison of present calculations with the PIM (*3*) is also discussed to see the importance of coulomb forces.

In the present analysis, the short-range force constants between the first three

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TABLE I

VALUES OF FORCE CONSTANTS IN UNITS OF K·dyne/cm

Force constants	$MnCr_2S_4$	$FeCr_2S_4$	$ZnCr_2Se_4$	$ZnCr_2O_4$
α_1	72.74	72.91	74.87	123.53
α_2	93.50	94.04	79.37	154.10
(α_2, α_2')	(83.50, 5.0)	(84.04, 5.0)	(69.37, 5.0)	(144.1, 5.0)
α_3	13.23	12.96	14.48	22.17

neighbors α_1, α_2, and α_3 (central) and α_1', α_2', and α_3' (corresponding angular) for the interatomic interactions Zn–O, Cr–O, and Cr–Cr, respectively, are evaluated by fitting the measured zone-center phonon frequencies (*5*) to the corresponding analytical expressions of A_{1g}, E_g, and ΣF_{1u}, obtained in Gupta *et al.* (*7*) by solving the dynamical matrix at $k = 0$ for an ideal spinel structure compound. The force constants thus calculated are listed in Table I along with the force constants of spinel sulfides (*8*).

A comparison of the values of force constants of oxide-spinel $ZnCr_2O_4$ and of chromium sulfide spinels indicates the following: (i) Similar to chromium sulfide spinel, the interatomic interaction α_2 of oxide spinel also dominates the other interatomic interactions, as octahedral bonding (Cr–O, ionic) is stronger than tetrahedral bonding (Zn–O, covalent) (*7*). (ii) The magnitudes of the interatomic interactions (α_1, α_2, α_3) of oxide-spinel $ZnCr_2O_4$ are larger compared with those of spinel-type chromium sulfides. (iii) It is also clear from Table I that if selenium from $ZnCr_2Se_4$ is replaced by oxygen ions ($ZnCr_2O_4$), the values of all force constants increase 1.65 times. This is because the unit-cell dimensions (bond lengths) of $ZnCr_2O_4$ are smaller than those in $ZnCr_2Se_4$ (*3*).

Initially, only central force constants are taken as input parameters to compute the zone-center phonon frequencies of Zn Cr_2O_4. To improve the agreement between the measured and theoretical phonon frequencies at the zone center, we incorporated the angular forces in the analysis also. It is found that first- and third-neighbor angular force constants (α_1', α_3') do not play any significant role; therefore, α_1' and α_3' are not included in our calculations. Most of the analytical expressions (*6*) involve the term $(\alpha_2 + 2\alpha_2')$, hence the value of α_2 is broken into the final α_2 and α_2' in such a manner that

TABLE II

MEASURED (*5*) AND CALCULATED ZONE-CENTER PHONON FREQUENCIES OF $ZnCr_2O_4$ ALONG WITH PIM AND SRM RESULTS OF HIMMRICH AND LUTZ (*3*)

	Frequency (cm^{-1})			
Species	Measured	Calculated with α_i, α_2', α_3	PIM	SRM
A_{1g}	692	692	690	679
E_g	457	457	456	474
F_{2g} (1)	610	631	614	610
F_{2g} (2)	515	552	529	513
F_{2g} (3)	186	159	181	164
F_{1u} (1)	624	629	620	620
F_{1u} (2)	506	513	500	522
F_{1u} (3)	372	348	375	374
F_{1u} (4)	186	194	189	202
A_{2u} (1)	—	695	677	701
A_{2u} (2)	—	391	446	520
Eu (1)	—	595	521	613
Eu (2)	—	329	142	307
F_{1g}	—	457	425	434
F_{2u} (1)	—	517	458	530
F_{2u} (2)	—	296	97	165

the final ($\alpha_2 + 2\alpha_2'$) equals the previous α_2. The values of the new α_2 and α_2' are adjusted so as to obtain better agreement. The final values of α_2 and α_2' are listed in parentheses in Table I. Using these values of α_1 (α_2, α_2') and α_3 from Table I, the zone-center frequencies for $ZnCr_2O_4$ have been calculated and are listed in Table II. The results thus obtained give better agreement with experiment as compared to the results with only central forces.

It is obvious from Table II that our short-range model provides fair agreement with the available experimental results as compared to the SRM of Himmrich and Lutz (*3*). Most of our calculated zone-center phonon modes agree with the results obtained by the PIM of Himmrich and Lutz (*3*) except for modes E_u (2) and F_{2u} (2). The present calculated values of E_u and F_{2u} differ considerably from the PIM results, because of the inclusion of the larger negative coulomb contribution to E_u (2) and F_{2u} (2) by Himmrich and Lutz (*3*). As experimental results for these modes are not available, a comparison cannot be made to identify the importance of coulomb forces to such an extent. Further experimental results are required to verify the importance of coulomb forces in oxide spinels.

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