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Optical Phonon Modes and Localized Effective Charges of Transition-Metal Dichalcogenides

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Reflection spectra have been measured in the far infrared region (10 cm^{-1}–500 cm^{-1}) for several kinds of crystals of transition-metal dichalcogenides (TX_2). Optical phonon frequencies of infrared active mode ($E \perp c$) are determined for the group IV compounds $HfSe_2$, $ZrSe_2$ and $TiSe_2$ and for the group VI compounds MoS_2, $MoSe_2$, WS_2 and WSe_2. Using available Raman data the localized effective charges (e_l^*) of these materials are estimated. The nature of the bonding in TX_2 is found to be well described in terms of the estimated e_l^* rather than by the macroscopic effective charge e_T^*.

§1. Introduction

The layered transition-metal dichalcogenides (TX_2) have been studied with continual interest for their anisotropic properties. The dichalcogenides of the group V elements, Nb and Ta, are known as two-dimensional metals showing the charge density wave (CDW) transitions, while most of the group IV–TX_2 such as ZrS_2 and the group VI–TX_2 such as MoS_2 are semiconductors or insulators.

It is of particular interest to know the nature of the chemical bonding in TX_2. It is expected from the crystalline configurations[1] and the mechanical property—they can be easily cleaved—that the intralayer forces are dominantly covalent and the interlayer forces are weak van der Waals one. The results of some band calculations[2,3] in fact indicate the covalent T–X bond in all these materials. On the other hand the tight-binding band calculation of Murray *et al.*[4] suggests that the bonding is ionic in the group IV compounds such as ZrS_2, HfS_2 and $HfSe_2$. Even the CDWs of the metallic TX_2 are considered to have profound relation with the chemical bonding, for as pointed out by Thompson the CDW transition temperatures show evident correlation with the ionicities of TX_2.[5]

The local T–X bonding will have most eminent effects on the properties of the lattice vibrations. So that the investigation of the lattice vibrational modes is expected to give important informations on the bonding nature. Especially that for the optical phonon modes will offer more direct information on the forces that work between T and X.

By the Raman experiments the low frequency rigid layer mode (E_{2g}^2) was observed in MoS_2[6] and the lattice mode degeneracy was identified between the Raman active E_{2g}^1 mode and the infrared active E_{1u} mode.[7] These facts indicate that the interlayer force is weak compared with the intralayer forces and support that the coupling between adjacent layers are probably through the van der Waals force.

In order to know the intralayer bonding it is necessary to estimate the amount of the charge transfer from the metal to the chalcogen atoms. We can estimate a few kinds of the effective charges from the infrared optical measurements. The most easily attainable quantity is the macroscopic (or transverse) effective charge (e_T^*) which is defined by the difference between the TO and LO phonon frequencies. Lucovsky *et al.*[8] estimated the e_T^* values for some group IV compounds and found that they are large and even larger than the formal valence number, 4, of these materials.

However such large e_T^* values does not directly mean the ionic bonding, since as was suggested by Burstein *et al.*,[9,10] the macroscopic effective charge is not the static charge localized at the atomic sites but it includes the nonlocalized charge. Instead they introduced the concept of the localized effective charge (e_l^*) which can be estimated from the reduction of the TO phonon frequency due to the local field effects induced by the localized

charge. Though e_l^* does not represent the static charge either, it was found that the localized effective charge has more intimate correlation with the ionicity of the bonding in the case of the diatomic crystals with cubic symmetry.[10]

In the present work we report the far infrared reflection spectra for the single crystals of the group IV compounds, $HfSe_2$, $ZrSe_2$ and $TiSe_2$, and the group VI compounds, WSe_2, $MoSe_2$, WS_2 and MoS_2. The analysis is made systematically for the infrared active phonon mode frequencies in terms of the reduced frequencies normalized by the characteristic frequencies. We show that we can estimate the localized effective charges also in the case of the layered TX_2 by use of the available Raman data. It is found that e_l^* is a good measure for the ionicity even in the case of these strongly anisotropic materials.

§2. Experimental Results

The single crystals of TX_2 were grown at about 900°C by the halogen vapor transport method. Bromine and iodine were used as a transport agent for the group VI and IV compounds respectively. Prereacted powder was sealed in a quartz tube ($25^{mm\phi}$) with halogen and was set for about 6 days in a furnace with temperature gradient of about 4°C/cm. The crystals were thin flat plates and the typical sample size was about $4^{mm} \times 4^{mm} \times 0.05^{mm}$ for the group VI compounds. The samples with larger area were obtained for the group IV compounds, however $TiSe_2$ and $ZrSe_2$ have the tendency to grow off stoichiometry with the form $T_{1+x}X_2$. We transported the crystals of $TiSe_2$ at 600°C to obtain as stoichiometric specimen as possible. According to Disalvo *et al.*[11] the deviation from 1:2 stoichiometry is fairly small at 600°C growth, perhaps excess Ti content $x<0.001$. $ZrSe_2$ was grown at both 600 and 800°C. Though completely stoichiometric samples were not obtained, the deviation x can be estimated to be smaller than 0.001 even for the sample grown at 800°C from the plasma frequency determined experimentally.

Reflection spectrum was measured at room temperature by a HITACHI model FIS 21 spectrometer which covers the spectral region 10 cm^{-1}–500 cm^{-1}. The reflectivity was measured at nearly normal incidence, ~13°, and an Cr-evaporated mirror was used as reference. Because of sample shape the measurements were restricted in the configuration $E \perp c$-axis.

For either polytype, $1T$ or $2H$, only one infrared active phonon mode exist that corresponds to the vibrational motion in the basal plane, E_{1u} for $2H$ and E_u for $1T$ polytype. Actually a single reststrahlen peak is observed at 385 cm^{-1} for MoS_2, 356 cm^{-1} for WS_2, 288 cm^{-1} for $MoSe_2$ and 248 cm^{-1} for WSe_2 as shown in Fig. 1. All the group VI compounds show very narrow reststrahlen band, that is, the difference between the frequency of the LO phonon (ω_{LO}) and that of the TO phonon (ω_{TO}) is small. This suggests that the bonding between the metal and the chalcogen atoms in a layer is dominantly covalent. The phonon peak positions are located just in the order of the reduced masses of the compounds.

On the other hand the compounds of the group IV metals exhibit very wide reststrahlen band. In Fig. 2 the spectra for $HfSe_2$ and $ZrSe_2$ are shown. The spectrum of $HfSe_2$ shows a wide reststrahlen band (120–210 cm^{-1}), which is almost the same as that reported earlier,[8] while the spectrum of $ZrSe_2$ is affected by the plasma of conduction carriers originated from the excess Zr atoms. In the figure the spectrum for the sample grown at 800°C is shown. The position of a plasma edge is shifted from 330 to 290 cm^{-1} for the

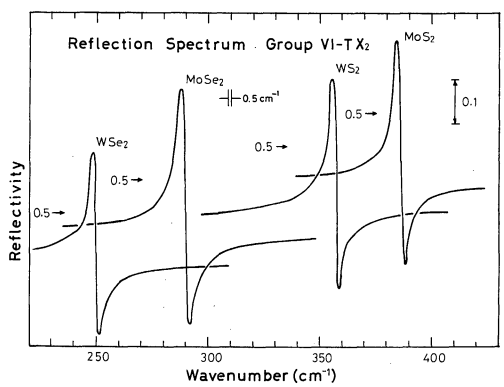

Fig. 1. Reflection spectra of the group VI compounds. Only one infrared active mode (E_{1u}) is observed for each compounds in the configuration $E \perp c$. The resolution is within 0.5 cm^{-1} for all the spectra.

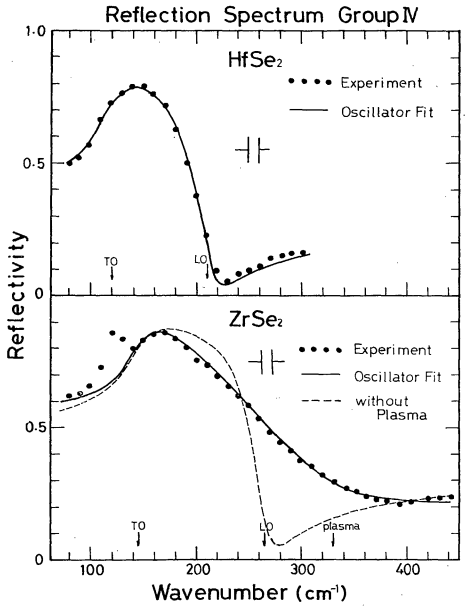

Fig. 2. Reflection spectra of the group IV compounds $HfSe_2$ and $ZrSe_2$. The spectrum of $ZrSe_2$ consists of three contributions, one infrared active mode (E_u), one plasma ($\omega_p'=330\,cm^{-1}$) and a phonon peak at $120\,cm^{-1}$ not clear in its origin.

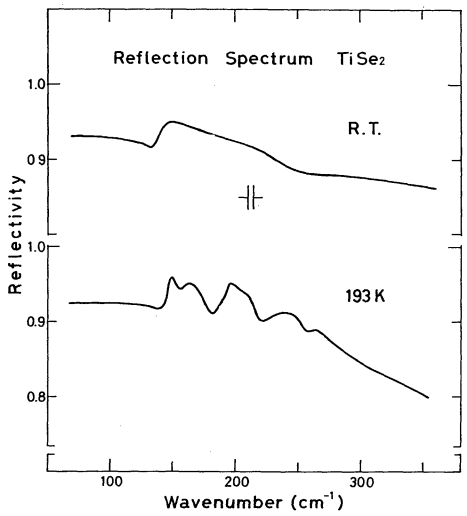

Fig. 3. Reflection spectra of $TiSe_2$. The spectra before (R. T.) and after (193 K) the phase transition ($T_0\simeq 200$ K) are shown.

sample grown at 600°C. A plasma frequency about $300\,cm^{-1}$ corresponds to the carrier density about $10^{18}\,cm^{-3}$ assuming the effective mass is equal to the free electron mass. If the excess Zr atoms supply one electron per atom to the conduction band, the excess Zr content can be estimated to be $x\lesssim 0.001$. The phonon parameters were determined through a conventional oscillator-fit procedure including a plasma contribution. The determined parameters are almost sample-independent and show large difference in the frequencies between ω_{LO} and ω_{TO} as in the case of $HfSe_2$.

The spectrum of $TiSe_2$ at room temperature shows the dominant contribution of free carriers (Fig. 3), for the reflectivity is high in the entire region. A plasma edge is observed at about $900\,cm^{-1}$ which is comparable with the value measured by Lucovsky *et al.*[12] for the crystal with 5% excess Ti, i.e. $Ti_{1.05}Se_2$. Since the crystal in the present experiment is nearly stoichiometric, this fact suggests that the existence of free carriers is intrinsic nature of $TiSe_2$ and is consistent with the DiSalvo's proposal that $TiSe_2$ is a semimetal.[11] The phonon parameters are determined in the same way as in $ZrSe_2$ case. The presence of two-carrier—electrons and holes—does not affect the fitting in the phonon spectral region and the fitting is good enough only to include a single carrier plasma with the plasma frequency $\omega_p'\simeq 900\,cm^{-1}$.* The determined phonon frequencies are nearly the same as those for $Ti_{1.05}Se_2$ by Lucovsky *et al.* and the difference between ω_{LO} and ω_{TO} is large in $TiSe_2$ as well as in $HfSe_2$ and $ZrSe_2$. A wide restrahlen band is also observed for the group IV sulphides, TiS_2, ZrS_2 and HfS_2, hence the large difference between ω_{LO} and ω_{TO} is considered to be intrinsic nature of the group IV compounds. This is equivalent to large values of the macroscopic effective charges e_T^* in the group IV compounds. The parameters are listed in Table I including those of the group IV sulphides which are cited from refs. 8 and 12.

As was pointed out also by Lucovsky *et al.*[8] in the case of MoS_2 and ZrS_2, it is worth noting that the TO phonon frequency of WSe_2 is about twice larger than that of $HfSe_2$ which has similar atomic reduced mass. Suppose the TO phonon frequency is determined by an effective force constant K_{eff}

* The frequency ω_p' corresponds to that at which a plasma edge is observed in the reflection spectrum. It is given by the density n, the effective mass m^* of conduction carrier and a dielectric constant ε_∞ as $\omega_p'=\sqrt{4\pi ne^2/m^*\varepsilon_\infty}$.

Table I. Parameters of the dispersion-analysis for the group IV and VI transition-metal dichalcogenides. The values for the starred materials are cited from refs. 8 and 12.

Specimens	Dielectric constant ε_∞	Phonon frequency TO(cm^{-1})	Phonon frequency LO(cm^{-1})	Oscillator strength S	Damping constant Γ(cm^{-1})	Effective charge e_T^*/e
1*T*-TiS_2^*	13.7	175	423	66.4	20.8	8.3
1*T*-$TiSe_2$	40	145	260	85	20	9
1*T*-ZrS_2^*	9.2	181	351	25.3	16.3	6.2
1*T*-$ZrSe_2$	12.0	145	265	28.1	22.0	7.2
1*T*-HfS_2^*	6.2	166	321	16.9	28.2	5.5
1*T*-$HfSe_2$	8.1	120	210	16.5	22.0	5.5
2*H*-MoS_2	15.2	384.3	387.3	0.2	1.7	1.2
2*H*-$MoSe_2$	18.0	286.9	290.9	0.5	2.2	1.7
2*H*-WS_2	17.0	354.5	358.0	0.3	2.2	1.5
2*H*-WSe_2	18.5	247.4	250.3	0.4	1.9	1.7

	Plasma frequency ω_p'(cm^{-1})	Damping constant γ(cm^{-1})
1*T*-$TiSe_2$	~900	$\sim 5 \times 10^2$
1*T*-$ZrSe_2$	330	5.0×10^2

between T and X atoms as defined by $\omega_{TO}=\sqrt{K_{eff}/\bar{m}}$, $\bar{m}$ being a reduced mass, then the difference in ω_{TO} is considered to be associated with that in the T–X interatomic effective force constant. The K_{eff} should depend on the interatomic distance r_0, so it is fair to compare the TO frequencies in terms of the reduced frequency $\bar{\omega}_{TO}=\omega_{TO}/\Omega_0$ normalized by a characteristic frequency $\Omega_0=\sqrt{e^2/\bar{m}r_0^3}$, which was demonstrared to be useful by Keyes.[13]

Figure 4(a) shows the plots of the TO phonon frequencies against Ω_0's for all the group IV and VI compounds. The group VI compounds are all on one straight line and the group IV compounds are also on another line except the Ti compounds. The same plots for the LO phonon frequencies are shown in Fig. 4(b). In this case they are all on the same single line except $TiSe_2$, and this means nearly equal reduced LO frequencies for all group IV and VI compounds.

We also measured the temperature dependence of the spectra for the above samples down to liquid nitrogen temperature. No essential change in the spectrum was observed except for one compound, $TiSe_2$. In $TiSe_2$ we found that below $T=200$ K there appear several fine structures (Fig. 3) and that they grow gradually as temperature is lowered to $T\simeq 160$ K and then diminish more gradually below 160 K. DiSalvo *et al.*[11] investigated neutron diffraction on $TiSe_2$ and revealed the structual phase transition at $T_0=202$ K and the existence of the commensurate superlattice below T_0. Therefore the spectral change observed in the present work is considered to correspond to that phase transition. Similar behavior is observed in the case of 1*T*–TaS_2 where the change in the far infrared spectrum occurs abruptly at the incommensurate-commensurate CDW transition temperature. For further details on $TiSe_2$ and for the relation between CDW and far infrared spectrum, we will report elsewhere.

§3. Estimation of Localized Effective Charge

All the group IV transition-metal dichalcogenides have large values of the macroscopic effective charge e_T^*. Perfect ionic bonding between the metal and the chalcogen atoms in one layer means the full charge transfer of four valence electrons. Such large e_T^*'s of the group IV–TX_2 seem to suggest an ionic bonding. However the macroscopic effective charge represents not only static charge transfer but also the contribution from the dynamical effects which is induced by the charge redistribution throughout the unit cell. For a typical example, trigonal Te has $e_T^*=2e$[14] in spite of its homopolar nature. As to the ionicity of TX_2, even the most ionic ones, Zr and Hf compounds, have the (Pauling's) fractional ionicities of at most

0.3, which is far small from the values indicating ionic bonding. Further the ionicities of Ti compounds are smaller than those of Zr and Hf compounds, although the e_T^* values of Ti compounds are rather large. This means that e_T^* is not a reasonable measure for the ionicity or covalency of the bonding in TX_2.

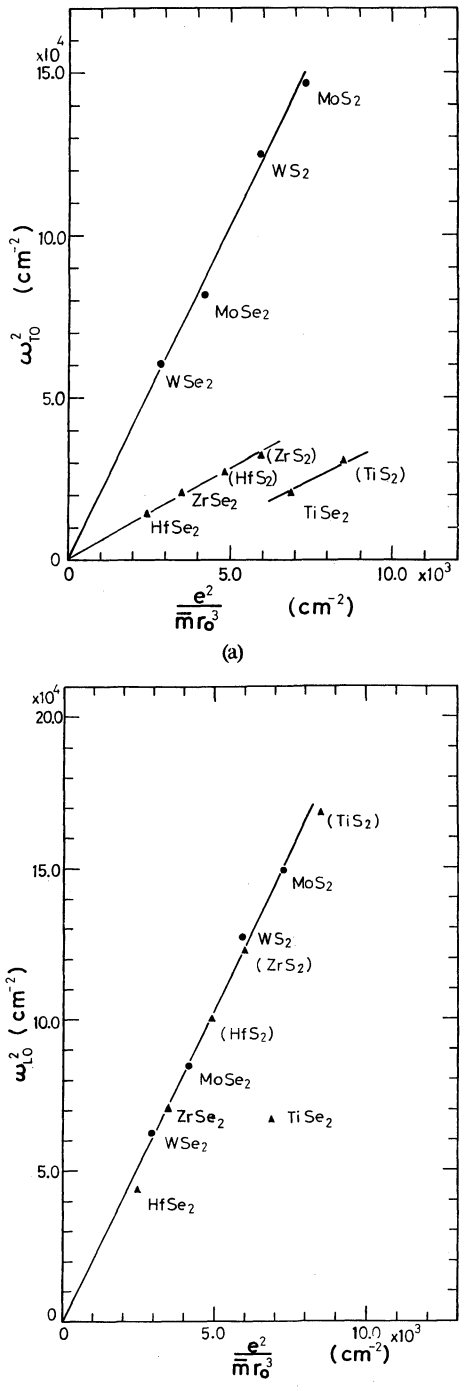

Fig. 4(a), (b). (a) Plots of ω_{TO} vs characteristic frequency $\Omega_0=\sqrt{e^2/\bar{m}r_0^3}$. (b) Plots of ω_{LO} vs Ω_0. The ω_{TO} and ω_{LO} values of the materials enclosed by the parentheses are from refs. 8 and 12.

Burstein *et al.*[9] suggested that the macroscopic effective charge e_T^* might be decomposed into the localized part e_l^* and the nonlocalized one e_{nl}^*,

$$e_T^*=e_l^*+e_{nl}^*. \tag{1}$$

According to them, e_l^* is essentially the localized moment generated per unit displacement of an ion. It induces the local field through dipole-dipole interaction and reduces the TO phonon frequency in the case of cubic diatomic crystals as

$$\omega_{TO}^2=\omega_0^2-\frac{4\pi N}{3\bar{m}}e_l^{*2}, \tag{2}$$

where the factor of 1/3 is the Lorentz local field factor reflecting the cubic symmetry and N is the ion pair density. The frequency ω_0 is the mechanical or spring-constant frequency and represents the contributions to ω_{TO} that arise from short range forces.

In order to evaluate e_l^* we must know the frequency ω_0 for each material. Lucovsky *et al.*[10] estimated ω_0 of the diatomic crystals with zincblende, Wurtzite or rocksalt structures from a simple force-constant model using available elastic constants. They found the trends that the localized effective charge scales well with the fractional ionicity in these materials. We expect the localized effective charge is also a good measure for describing the covalency or ionicity of the bonding in the transition-metal dichalcogenides. Though there are no available data for the elastic constants of TX_2 to calculate ω_0, we can find different method to deduce the value of ω_0 in this case.

In the case of TX_2 there is a certain vibrational mode which is managed with the same force-constant as in the infrared active TO phonon mode but with no local moment being induced. Such mode is Raman active and was really observed for some of TX_2. In the $1T$ polytype this is the mode designated by the irreducible representation E_g (Fig. 5). If the force constant between T and X is K and no other forces, such as Lorentz dipolar force or interlayer interaction, work on, then

the frequencies of the infrared active E_u and the Raman active E_g modes are respectively given by

$$\omega_0(E_u)=\sqrt{K(2m_X+m_M)/2m_Xm_M}, \quad (3)$$

$$\omega_0(E_g)=\sqrt{K/2m_X}. \quad (4)$$

So that the following relation is obtained

$$\omega_0(E_u)=\omega_0(E_g)\sqrt{1+2m_X/m_M}. \quad (5)$$

The localized moment is not induced by the vibrational motion of the E_g mode since it is infrared inactive due to the inversion symmetry of the system. So that no reduction in the E_g mode frequency occurs due to the local field effects, and the observed Raman frequency $\omega(E_g)$ is expected to coincide with $\omega_0(E_g)$. On the other hand the infrared active E_u mode induces the localized moment. If we use the representation e_l^* also in this case as a measure of the moment, then the E_u mode frequency may be expressed as[15]

$$\omega^2(E_u)=\omega_0^2(E_u)-\frac{4\pi N}{L^{-1}\bar{m}}e_l^{*2}, \quad (6)$$

where N is the density of the TX_2 formula unit and L is the Lorentz factor which takes different value for each material.* The frequency $\omega_0(E_u)$ is related to $\omega_0(E_g)$ by the eq. (5), thus in this case both ω_0 and ω_{TO} are observable through the Raman and infrared spectra. The e_l^* values can be obtained by the above equation and are listed in Table II using the Raman data by Smith *et al.*[16]

In the case of the group VI compounds with $2H$ polytype, the TO phonon is assigned to the infrared active E_{1u} mode. There are three basal plane Raman mode designated by E_{2g}^1, E_{2g}^2 and E_{1g}. The atomic displacements of these modes are shown in Fig. 5. The E_{2g}^1 mode is known as the rigid layer mode, the E_{2g}^1 mode differs from the E_{1u} mode only by an interlayer phase shift of 180° and in this case the E_{1g} mode is considered to correspond to the E_g mode in the $1T$ case. For $2H$–MoS_2 the frequency of the rigid layer mode E_{2g}^2 was found to be very low[6] and the lattice mode degeneracy between E_{2g}^1 and E_{1u} was

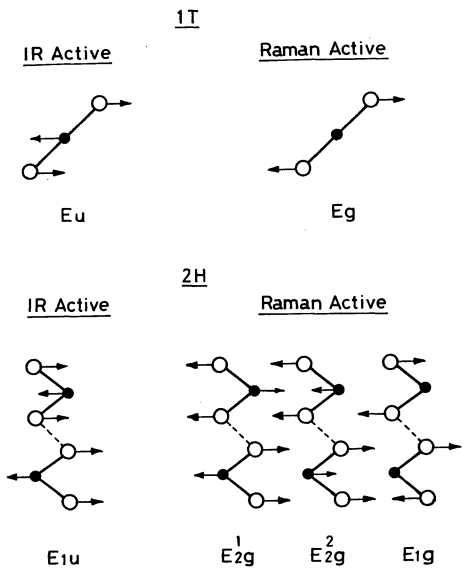

Fig. 5. Vibrational motions for the infrared and Raman active modes in the $2H$ and $1T$ polytypes. Only those are shown with displacement vectors parallel to the layer.

really identified.[7] These indicate that the interlayer interaction is weak compared to the intralayer interactions in MoS_2. Hence the interlayer interaction is considered to be also weak for other group VI compounds. Under this condition the frequency of the E_{1g} mode can be expressed by the same formula as eq. (4), since the E_{1g} mode does not induce the localized moment either in the $2H$ case. As a result the spring-constant E_{1u} mode frequency, $\omega_0(E_{1u})$, which is also described by the eq. (3), has the same relation to $\omega_0(E_{1g})$ or $\omega(E_{1g})$ as described by eq. (5).

However there are no available Raman data in the case of group VI compounds except those for MoS_2. The ω_0 value estimated from the frequency of the E_{1g} mode observed by Agnihotri *et al.*[17] is only slightly larger than ω_{TO}, accordingly the e_l^* value is very small $e_l^*/e=0.2$. In order to guess the e_l^* value of the other group VI compounds, we take ω_{LO} for ω_0, since ω_{LO} is expected to have not so deviated value from that of ω_0. The LO phonon frequency can be expressed in terms of e_T^*, e_l^* and ω_0 in the reduced form

$$\bar{\omega}_{LO}^2=\bar{\omega}_0^2-\frac{4\pi Nr_0^3}{e^2}(e_l^{*2}/L^{-1}-e_T^{*2}/\varepsilon_\infty). \quad (7)$$

The second term is considered to be much

* The system is assumed to be an anisotropic 3D one—not 2D—characterized by one parameter c/a, and the Lorentz factors are obtained as a monotonic function of c/a using the graph in ref. 15.

Table II. Phonon frequencies and reduced phonon frequencies for the group IV and VI transition-metal dichalcogenides. Estimated frequencies ω_0 and two types of effective charges are also listed. The values in the parentheses are estimated from the Raman data in ref. 17.

	$\omega_{TO}(cm^{-1})$	$\omega_{LO}(cm^{-1})$	$\omega_0(cm^{-1})$	$\bar{\omega}_{TO}$	$\bar{\omega}_{LO}$	$\bar{\omega}_0$	e_T^*/e	e_l^*/e
TiS_2^*	175	423	355	1.90	4.59	3.85	8.3	2.2
$TiSe_2$	145	260	279	1.7	3.1	3.37	9.2	2.1
ZrS_2^*	181	351	308	2.34	4.53	3.97	6.2	2.4
$ZrSe_2$	145	265	245	2.43	4.45	4.11	7.2	2.5
HfS_2^*	166	321	295	2.38	4.59	4.22	5.5	2.6
$HfSe_2$	120	210	213	2.40	4.19	4.25	5.5	2.6
MoS_2	384.3	387.3	387.3 (385.0)	4.50	4.54	4.54 (4.51)	1.2	0.4 (0.2)
$MoSe_2$	286.9	290.9	290.9	4.46	4.52	4.52	1.7	0.5
WS_2	354.5	358.0	358.0	4.62	4.67	4.67	1.5	0.4
WSe_2	247.4	250.3	250.3	4.58	4.65	4.65	1.7	0.5

smaller than the first term, since $e_T^{*2}/e^2\varepsilon_\infty$ is small for all the group VI compounds and e_l^{*2}/e^2 is expected to be also small as in the case of MoS_2. In the cubic diatomic crystals and also in the group IV–TX_2, as shown earlier, the ω_{LO} value is always larger than the ω_0 value. Thus the estimated e_l^* value using ω_{LO} for ω_0 will give an upper limit value, which is listed in the Table II. The value $e_l^*/e \simeq 0.5$ is obtained for all the group VI compounds. Since the 'true' e_l^* value is probably smaller than this value, we can guess that the localized effective charge of the group VI–TX_2 is much smaller than the formal valence $4e$ and than the e_l^* values of the group IV–TX_2.

§4. Discussions

The estimated frequencies ω_0 (or ω_{LO} in the case of the group VI–TX_2) are plotted in Fig. 6 against Ω_0. As ω_0 gives a measure for the magnitude of the spring-constant, the figure tells that the group IV– and VI–TX_2 are classified into three groups in a 'mechanical' sense and that in each group the spring-constant is nearly equal.† When we compare the ω_0 values with ω_{TO} values which are also plotted in the same figure, the values of the localized effective charges, defined by the difference between ω_0 and ω_{TO}, are found to be equal in each group.

The e_l^* values for the Zr and Hf compounds are approximately equal, $e_l^* \simeq 2.5e$, in contrast to their e_T^* values, which range from $5.5e$ for $HfSe_2$ to $7.2e$ for $ZrSe_2$. It can be said that the value $e_l^*/e = 2.5$ is not unreasonable considering that the fractional ionicity is about 0.3 and that it is smaller than the formal valence number 4.

The e_l^* values of TiS_2 and $TiSe_2$ are estimated to be $2.2e$ and $2.1e$ respectively. They are rather small compared with those of the Zr

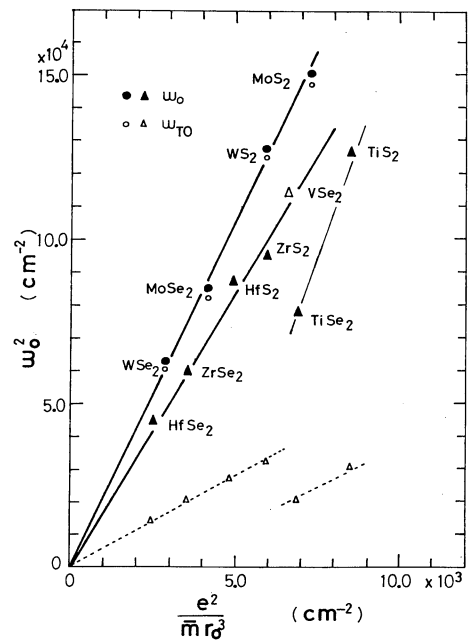

Fig. 6. Plots of ω_0 vs Ω_0. The estimated values of ω_0 are indicated by the closed triangles (1*T* polytype) and the closed circles (2*H* polytype). The ω_{TO} values are also shown by the open triangles and open circles. The ω_0 values of the group V compound 1*T*-VSe_2 is estimated from the Raman data by Smith *et al.*[18]

† It is curious to note that the ω_0 value of the group V compound 1*T*-VSe_2 is also equal to that for the Zr and Hf compounds.[18]

and Hf compounds, but it is consistent with the ionicity, for the fractional ionicities of the Ti compounds are about 0.2. If we remember that the e_T^* values are largest for the Ti compounds, the result means the non-localized charge contribution is dominant in these materials and that the large charge redistribution occurs by the lattice vibrational motions of the constituent atoms. This may be attributed to the semimetallic band structure or to the resultant electron-hole (or CDW) instability.[11]

The group VI transition metals Mo and W have almost the same electronegativities as those of the chalcogen atoms S and Se.[19] Therefore the fractional ionicities of these compounds are very small, and this is consistent with the small values of e_l^*.

The results are collected in Table II and the relation between the estimated e_l^* values and the Pauling's fractional ionicities is shown in Fig. 7. The plots show good correlation between both quantities and from this we can expect that the localized effective charges give a better measure for the ionicity or covalency of the bonding in TX_2.

Finally we consider the trends of the LO phonon frequencies in TX_2. In Fig. 4 we find both the group IV and VI compounds have almost the same reduced LO phonon frequencies except $TiSe_2$. Though we can find no appropriate explanation for this fact, the equal values of ω_{LO} in each group are considered to be based on the equal values of the reduced spring-constant frequency in each group as shown in Fig. 6. This is evident for the group VI compounds. In this case ω_{LO} is considered to be nearly equal to ω_0 since the second term in eq. (7) is very small because of the small values of e_T^* and e_l^* and of the large values of ε_∞. In the case of the group IV compounds the second term in eq. (7) is somewhat large, so the constant value of ω_{LO} may be attributed to the trends in e_T^* that it is proportional to the dielectric constant[12] as well as to the constancy of the $\bar{\omega}_0$ and e_l^* values.

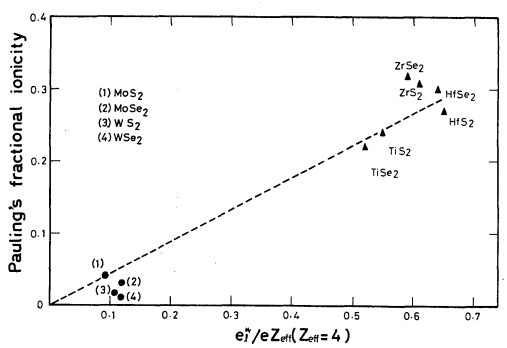

Fig. 7. Pauling's fractional ionicities vs the estimated localized effective charges. The effective charges are normalized by the formal valence number 4.

As a summary, we can guess from the e_l^* values of TX_2 that the rather large e_T^* values of the group IV compounds are not due to large static charge transfer from the metal to the chalcogen atoms but the dominant contribution to e_T^* is from the nonlocal charges which are perhaps associated with the 'resonance' bonding.[14] This is also consistent with the band calculations by Mattheiss[2] and by Kasowski[3] which indicated the covalent bonding and the unlikeliness of such large charge transfer. The values e_l^*'s of the group VI compounds are found to be almost zero which support firmly that the bonding is strongly covalent.

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