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Lattice vibrations in $A^IB^{III}C_2^{VI}$ chalcopyrite compounds

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In honor of Emanuel Mooser's 60th birthday

Abstract. In a simplified version of the extended Keating model with bond-bending forces neglected analytical relations are derived for all optical vibrational modes of the chalcopyrite lattice. The theoretical results are compared with experimental data. The influence of the noble metal *d* electrons on the force constants is discussed.

1. Introduction

In recent years, numerous experimental studies of the long-wavelength lattice vibrational modes of the $A^IB^{III}C_2^{VI}$ chalcopyrite semiconductors have been reported in the literature ([1, 2] and references therein). However, if the results of different authors are compared with each other one finds that there are partly considerable discrepancies in the symmetry assignment of the mode frequencies found experimentally. In the case of infrared reflectivity spectra it has been established that most of the confusion is due to mode leakage effects caused by imperfect polarization conditions in the measurements [3, 4]. Difficulties arise also in the interpretation of Raman scattering data due to the appearance of modes in forbidden polarizations and, partly, the occurrence of comparatively strong second-order features in the spectral range of the fundamental lattice modes [5]. Obviously, the identification of modes with low scattering efficiencies becomes difficult under these conditions. For this reason, in some previous studies attempts have been made to look for correlations and trends in the zone-centre mode frequencies in order to facilitate the correct interpretation of experimental spectra. These considerations based either on a tetra-atomic linear chain model [3, 6–9] or a comparison with the lattice modes in the binary sphalerite-structure analogs of the ternary compounds using the folding-back method [1, 6, 10] led to a quite satisfactory description of trends in the infrared active vibrational modes with highest energy, but all conclusions made with regard to modes with lower energies remained rather speculative. More realistic three-dimensional calculations of zone-centre optical mode frequencies have been made using a rigid-ion model [11], a Urey–Bradley force field [12] and an extended Keating model [13–15]. However, although the emphasis of these investigations was on the interpretation of experimental data for specific compounds it has been found that within the theoretical models used so far no consistent description of all the mode frequencies of a given compound can be achieved. Moreover, because of the large number of parameters involved these models are too unhandy to find out any correlations or trends in the mode frequencies.

In the present work we describe a simplified version of the Keating model which enables us to derive analytical relations for the frequencies of all optical modes of the chalcopyrite lattice and, thus, to consider correlations between optical modes of different symmetry in a specific compound as well as trends in the mode frequencies within the whole compound family. It is shown that most of the discrepancies between theory and experiment found in previous calculations [11–15] can be removed if the contribution of long-range Coulomb forces to the phonon energies is taken into account. Finally, interatomic force constants are determined from experimental data and compared with corresponding results for sphalerite-structure diatomic compounds.

2. The Keating model

The $\mathrm{C^{VI}A_2^{I}B_2^{III}}$ tetrahedral unity of the chalcopyrite lattice and the force constants to be introduced in the Keating model are shown in Fig. 1. The fractional positional coordinates of the atoms are A_1 (0, 0, 0), A_2 (0, 1/2, 1/4), B_1 (1/2, 0, 1/4), B_2 (1/2, 1/2, 0) and C_1 (x, 1/4, 1/8). In general, the lattice parameter ratio c/a and the free parameter x differ from the values $c/a = 2$ and $x = 1/4$ for the ideal chalcopyrite lattice [16, 17]. Therefore, besides the two central (bond-stretching) force constants α_A and α_B describing the interaction between nearest neighbours one has to introduce five different noncentral (bond-bending) force constants β_1', β_1'', β_2', β_2'', and β_3 describing the interaction between second-nearest neighbours. Under these general assumptions the resulting dynamical matrix can be solved only numerically.

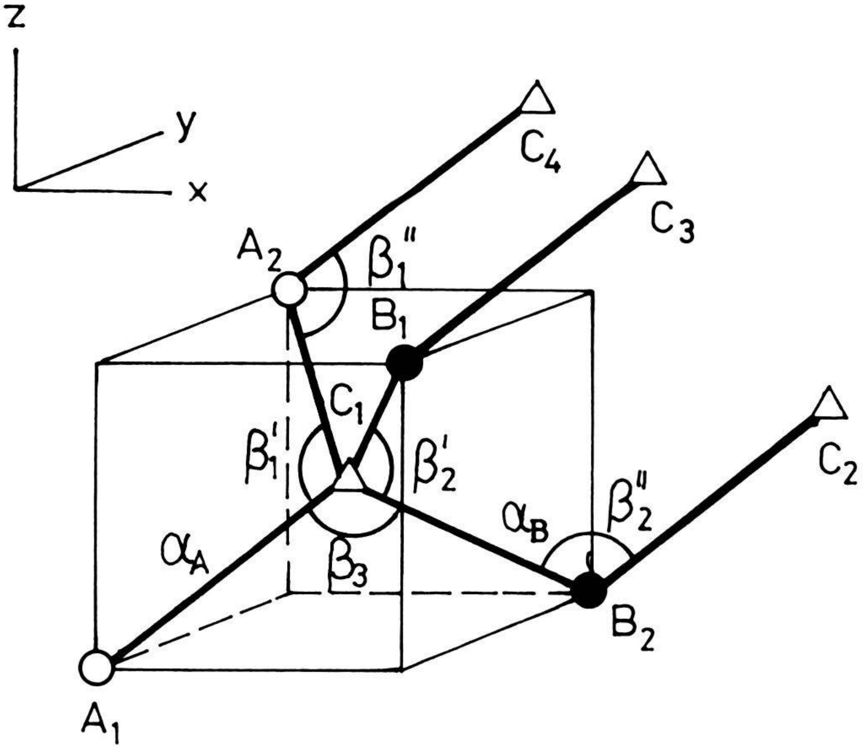

Figure 1
Basis of the chalcopyrite lattice

Let us now consider the possibilities for additional justified approximations to simplify the problem. Firstly, looking at the structure parameters of the $A^IB^{III}C_2^{VI}$ compounds reported so far it is obvious that the lattice parameters a and c of most of the compounds have been measured with sufficient accuracy [16–18]. However, with regard to the free parameter x the experimental information is limited to few compounds only and even in these cases partly contradictory [19]. Thus, since (i) a correct consideration of the influence of x on the phonon spectra cannot be made in most of the compounds and (ii) the influence of the c/a ratio on the phonon energies is expected to be of the same order of magnitude as that of the free parameter x we generally neglect the deviation from the ideal chalcopyrite lattice and assume $c/a = 2$ and $x = 1/4$. If we follow the Keating model considerations for the sphalerite-structure binary compounds [20] this supposition implies also a reduction in the number of the independent bond-bending force constants from five to two ones, namely $\beta_1 = \beta_1' = \beta_1''$ and $\beta_2 = \beta_2' = \beta_2''$ with $\beta_3 = (\beta_1 + \beta_2)/2$. Secondly, in analysing the lattice vibrational properties of the sphalerite-structure $A^{III}B^V$, $A^{II}B^{VI}$ and A^IB^{VII} compounds it has been found that the bond-bending force constants follow the proportionality $\beta \sim (1-f_i)\alpha$ [20, 21] where f_i is the spectroscopic bond ionicity according to Phillips and van Vechten [22]. A comprehensive numerical analysis of all existing experimental data for these compounds showed that within an accuracy of ±10% the bond-bending force constants are given by [21]

$$\beta = 0.25(1-f_i)\alpha. \tag{1}$$

Now, assuming that relation (1) remains valid in the $A^IB^{III}C_2^{VI}$ compounds and accounting for the relatively large ionicities of $f_{i,AC} = 0.77$–0.86 and $f_{i,BC} = 0.51$–0.65 for the A^I–C^{VI} and B^{III}–C^{VI} bonds, respectively, of these compounds [23] it is obvious that the bond-bending force constants will be small if compared with the bond-stretching force constants. Therefore, it can be suggested that at least for the high-energy optical modes the frequencies of which are essentially determined by bond-stretching forces the influence of the bond-bending force constants on the phonon energies will be rather small and is, may be, of the same order of magnitude as that caused by the deviation of the true c/a and x values from the ideal chalcopyrite. Thus, the assumption $\beta_1 = \beta_2 = 0$ should be a good first approximation in evaluating the mode frequencies.

If these suppositions are made the dynamical matrix can be solved analytically. According to group theory the irreducible representation of the 21 optical phonon normal modes at the centre of the Brillouin zone is given by $1A_1 + 2A_2 + 3B_1 + 3B_2 + 6E$ where the A_1, B_1, B_2 and E modes are Raman active, the B_2 and E modes are infrared active for incident radiation polarized parallel and perpendicular, respectively, to the tetragonal c axis of the crystals and the A_2 modes are optically inactive. The corresponding analytical relations for the frequencies of these modes are

$$\omega^2(A_1) = \frac{2(\alpha_A + \alpha_B)}{m_C}, \tag{2}$$

$$\omega^2(A_2^1) = \frac{4\alpha_B}{m_C}, \qquad \omega^2(A_2^2) = \frac{4\alpha_A}{m_C}, \tag{3}$$

$$\omega^2(E^1) = \omega^2(B_2^1) = 4\alpha_B\left(\frac{1}{m_B} + \frac{1}{m_C}\right), \tag{4}$$

$$\omega^2(E^2)=\omega^2(B_1^1)=\alpha_A\left(\frac{2}{m_A}+\frac{1}{m_C}\right)+\alpha_B\left(\frac{2}{m_B}+\frac{1}{m_C}\right)$$
$$+\left\{\left[\alpha_A\left(\frac{2}{m_A}+\frac{1}{m_C}\right)-\alpha_B\left(\frac{2}{m_B}+\frac{1}{m_C}\right)\right]^2+\frac{4\alpha_A\alpha_B}{m_C^2}\right\}^{1/2}, \tag{5}$$

$$\omega^2(E^3)=\omega^2(B_2^2)=4\alpha_A\left(\frac{1}{m_A}+\frac{1}{m_C}\right), \tag{6}$$

$$\omega^2(E^4)=\omega^2(B_1^2)=\alpha_A\left(\frac{2}{m_A}+\frac{1}{m_C}\right)+\alpha_B\left(\frac{2}{m_B}+\frac{1}{m_C}\right)$$
$$-\left\{\left[\alpha_A\left(\frac{2}{m_A}+\frac{1}{m_C}\right)-\alpha_B\left(\frac{2}{m_B}+\frac{1}{m_C}\right)\right]^2+\frac{4\alpha_A\alpha_B}{m_C^2}\right\}^{1/2}, \tag{7}$$

$$\omega^2(E^5)=\omega^2(E^6)=\omega^2(B_1^3)=\omega^2(B_2^3)=0. \tag{8}$$

Here, m_A, m_B and m_C are the masses of the A^I, B^{III} and C^{VI} atoms, respectively. Further, to facilitate the forthcoming discussion different modes of equal symmetry are marked with an upper index which increases with descending frequency. In fixing the mode sequences it is taken into account that $\alpha_B > \alpha_A$ [12–15].

On the basis of the relations (2) to (8) three interesting conclusions can be immediately made. Firstly, it follows from (8) that nonvanishing frequencies of the low-energy modes E^5, E^6, B_1^3 and B_2^3 can only be achieved if bond-bending forces are included. Certainly, if an exact theoretical description of the frequencies of these modes is desired one has to use the general formulation of the Keating model with five different bond-bending force constants and to account for the true values of the lattice parameter ratio c/a and the free parameter x. This result also explains the failure of previous theoretical studies in deriving the frequencies of these modes because mostly the calculations have been made using a reduced number of bond-bending force constants and assuming $c/a = 2$ and $x = 1/4$ [11–15]. Secondly, we see from (4) that the E^1 and B_2^1 infrared active modes are sphalerite-like in nature and are determined by the properties of the B^{III}–C^{VI} sublattice alone. Except for slight changes due to bond-bending forces the frequencies of these two modes are equal in a given compound, and if changes in the α_B can be neglected they are also equal in all compounds with the same B^{III}–C^{VI} sublattice. The latter conclusion is also true for the A_2^1 mode (see relation (3)). Thirdly, it can be seen from relations (3) and (6) that completely the same behaviour must be expected for the E^3, B_2^2 and A_2^2 modes with the only exception that here the A^I–C^{VI} sublattice plays the decisive role.

Relations (5) and (7) suggest the conclusion that in a specific compound the frequencies of the E^2 and B_1^1 modes on the one hand and of the E^4 and B_1^2 modes on the other hand are equal in magnitude. However, this supposition is wrong because (5) and (7) give indeed the true frequencies of the B_1 modes but only the mechanical or spring-constant frequencies for the infrared active E modes which differ from the transverse and longitudinal mode frequencies. If the force constants α_A and α_B are empirically determined from experimental values for the frequencies of modes which are only Raman active or inactive we do not derive pure short-range force constants but force constants which already implicitly account for the influence of long-range Coulomb forces on the vibrational properties of the crystal. Now, in the case of infrared active modes the local atomic displacements give rise to a nonvanishing net dipole momentum per unit cell and, thus, to additional dipole–dipole interactions which are absent for modes which are inactive or only Raman active. It has been shown in [24] that the influence of these dipole–dipole interactions on the transverse optical mode frequencies can be described in terms of a so-called localized effective charge e_L^* which in a simple manner depends on the bond ionicity and the formal valence of the constituent atoms of the crystal. In evaluating the true transverse optical mode frequency one can use the same relation as for the spring-constant frequency if the mechanical force constant α_i is replaced by a reduced force constant $\alpha_i' = \alpha_i - \Delta\alpha_i$ [21, 24]. If the results obtained for the sphalerite-structure binary compounds are extended to the ternary chalcopyrite crystals we have to introduce two independent localized effective charges e_{LA}^* and e_{LB}^* characteristic of the $\mathrm{A^I}$–$\mathrm{C^{VI}}$ and $\mathrm{B^{III}}$–$\mathrm{C^{VI}}$ bonds, respectively. In complete analogy to the model proposed for diatomic crystals [21, 24] we assume that $\Delta\alpha_A$ and $\Delta\alpha_B$ are given by

$$\Delta\alpha_i = \frac{\sqrt{3}(e_{Li}^*)^2}{16\varepsilon_v d_i^3}, \qquad i = A, B \tag{9}$$

where ε_v is the permittivity of free space and d_A and d_B are the $\mathrm{A^I}$–$\mathrm{C^{VI}}$ and $\mathrm{B^{III}}$–$\mathrm{C^{VI}}$ bond lengths. Now, returning to the starting point of this discussion we see that the frequencies of the transverse E^2 and E^4 modes will be always below the frequencies of the B_1^1 and B_1^2 modes, respectively.

In conclusion, some remarks regarding the applicability of the tetra-atomic linear chain model. If k_A and k_B are the force constants of the model one obtains one Raman active mode with a frequency of

$$\omega_1^2 = \frac{k_A + k_B}{m_C} \tag{10}$$

and two infrared active optical modes with frequencies of

$$\begin{aligned}\omega_{2,3}^2 = {} & k_A\left(\frac{1}{m_A} + \frac{1}{2m_C}\right) + k_B\left(\frac{1}{m_B} + \frac{1}{2m_C}\right) \\ & \pm\left\{\left[k_A\left(\frac{1}{m_A} + \frac{1}{2m_C}\right) - k_B\left(\frac{1}{m_B} + \frac{1}{2m_C}\right)\right]^2 + \frac{k_A k_B}{m_C^2}\right\}^{1/2}\end{aligned} \tag{11}$$

where as before the m_A, m_B and m_C are the masses of the constituent atoms of the compound [6]. If these relations are compared with those derived in the present study we see that they exactly correspond to the relations (2), (5) and (7) for the A_1, E^2 and E^4 modes, respectively, if one sets $k_A = 2\alpha_A$ and $k_B = 2\alpha_B$. In most of the previous studies the frequency ω_2 of the linear chain model has been identified with the frequencies of the E^1 and B_2^1 modes [3, 6, 7, 9]. Obviously, this supposition is wrong, and all conclusions concerning trends in the lattice vibrational modes of the chalcopyrite compounds made on the basis of this assumption must be reconsidered.

3. Comparison with experiment

First let us consider the frequencies of the transverse E^1 and B_2^1 modes which have been measured in most of the $\mathrm{A^IB^{III}C_2^{VI}}$ compounds. It can be seen from

Table 1
Frequencies (in cm^{-1}) of the E^1_{TO} and $B^1_{2\mathrm{TO}}$ modes and derived values for the force constant α_B (in N/m)

Compound	$\bar{\nu}(E^1_{\mathrm{TO}})$	$\bar{\nu}(B^1_{2\mathrm{TO}})$	Ref.	α_B
$CuAlS_2$	444	446	[13]	62.2
$CuAlSe_2$	—	364	[25]	56.6
$CuGaS_2$	367	367	[26]	58.4
$AgGaS_2$	368	367	[13]	59.1
$CuGaSe_2$	250	254	[27]	47.8
$AgGaSe_2$	250	248	[10]	46.9
$CuGaTe_2$	≈209		[7]	≈38
$AgGaTe_2$	204	198	[28]	35.9
$CuInS_2$	324	328	[4]	53.1
$AgInS_2$	325	325	[29]	54.1
$CuInSe_2$	213	214	[30]	44.7
$AgInSe_2$	215	208	[31]	43.6
$CuInTe_2$	167	168	[32]	35.3
$AgInTe_2$	166	168	[31]	34.6

Table 1 that the frequencies of these modes are indeed equal in a given compound and also in compounds having the same B^{III} and C^{VI} atoms as constituent elements as expected from relation (4). The small differences of a few cm^{-1} only can be ascribed to the influence of bond-bending forces. Experimental results for the frequencies of the transverse E^3 and B^2_2 modes are compiled in Table 2. Although the experimental uncertainties in these frequencies are larger than in the case of the E^1 and B^1_2 modes [2] it is obvious that these mode frequencies are nearly equal in a given compound and also nearly equal in compounds containing the same A^I and C^{VI} atoms. This result confirms the sphalerite-like nature of these modes predicted by relation (6). The only exception is $CuInS_2$ for which the E^3_{TO} and $B^2_{2\mathrm{TO}}$ mode frequencies are below the corresponding frequencies in $CuAlS_2$ and $CuGaS_2$ (see Table 2). This result is due to the fact that the Cu–S bond length in $CuInS_2$ is distinctly larger than in $CuAlS_2$ and $CuGaS_2$ [17] which gives rise to a decrease in the force constant α_A and, therefore, also in the E^3_{TO} and $B^2_{2\mathrm{TO}}$ mode frequencies.

In order to verify the validity of the relations (2), (3), (5) and (7) for the other

Table 2
Frequencies (in cm^{-1}) of the E^3_{TO} and $B^2_{2\mathrm{TO}}$ modes and derived values for the force constant α_A (in N/m)

Compound	$\bar{\nu}(E^3_{\mathrm{TO}})$	$\bar{\nu}(B^2_{2\mathrm{TO}})$	Ref.	α_A
$CuAlS_2$	265	269	[13]	33.3
$CuGaS_2$	262	262	[13]	32.4
$CuInS_2$	244	238	[4]	28.1
$CuGaSe_2$	—	178	[27]	24.7
$CuInSe_2$	179	181	[30]	25.8
$AgGaS_2$	213	213	[26]	27.1
$AgGaSe_2$	159	154	[10]	24.9
$AgInSe_2$	153	149	[31]	24.1
$AgGaTe_2$	134	130	[28]	22.7
$AgInTe_2$	130	131	[31]	22.0

optical modes values for the force constants α_A and α_B and for the localized effective charges e_{LA}^* and e_{LB}^* are required. Obviously, to determine these model parameters from experimental data, besides the frequencies of the transverse optical modes given in Tables 1 and 2 we need the frequencies of two only Raman active modes. So far, Raman scattering measurements have been reported for $CuAlS_2$, $CuGaS_2$, $CuInS_2$, $CuGaSe_2$, $AgGaS_2$ and $AgGaSe_2$. However, even in the most extensively studied compounds $CuGaS_2$ and $AgGaS_2$ only the A_1 mode frequency has been identified with certainty whilst the B_1 mode frequencies scatter widely from author to author. For this reason, another approach is used to derive the force constants α_A and α_B. A detailed analysis of the lattice vibrational properties of the sphalerite-structure $A^{III}B^V$, $A^{II}B^{VI}$ and A^IB^{VII} compounds showed that in these crystals the localized effective charge can be estimated within an accuracy of about ±10% using the relation $e_L^* = 0.28 f_i\ (Z_A + Z_B)$ [21]. Here, f_i is again the spectroscopic bond ionicity and Z_A and Z_B are the formal valencies of the A and B atom, respectively. Since no other information is available regarding the magnitude of the localized effective charges in the $A^IB^{III}C_2^{VI}$ compounds we assume that this relation for e_L^* remains valid in the ternary compounds, too. Then, we have

$$e_{LA(B)}^* = 0.28 f_{i,AC(BC)}(Z_{A(B)} + Z_C) \qquad (12)$$

with $Z_A = 1$, $Z_B = 3$ and $Z_C = 2$. The bond ionicities $f_{i,AC}$ and $f_{i,BC}$ of the $A^IB^{III}C_2^{VI}$ compounds can be taken from [23].

Now, using relations (4), (6), (9) and (12) and accounting for the A^I–C^{VI} and B^{III}–C^{VI} bond lengths given in [17] the force constants α_A and α_B can be evaluated from the frequencies of the sphalerite-like modes given in Tables 1 and 2. The resulting α_A and α_B values are compiled in Tables 1 and 2, too.

With these force constants we have calculated the frequencies of the E_{TO}^2, E_{TO}^4, A_1, B_1^1 and B_1^2 modes using relations (2), (5) and (7). A comparison with experimental data reported in the literature is given in Tables 3 and 4. Accounting for the approximations made in evaluating the force constants the agreement between calculated and experimental frequencies for the E_{TO}^2 and E_{TO}^4 modes (Table 3) as well as for the A_1 modes (Table 4) is surprisingly good. In most cases, the discrepancy between theory and experiment found here is smaller than in the more elaborate theoretical studies reported previously [12–15], in particular with regard to the A_1 modes. This result justifies the assumptions made in the present work.

Table 3
Comparison of calculated and experimental frequencies (in cm^{-1}) of the E_{TO}^2 and E_{TO}^4 modes

Compound	$\bar{\nu}(E_{TO}^2)$ calc.	exp.	Ref.	$\bar{\nu}(E_{TO}^4)$ calc.	exp.	Ref.
$CuAlS_2$	402	433	[13]	195	218	[13]
$CuGaS_2$	325	332	[26]	168	167	[26]
$CuInS_2$	285	295	[4]	142	140	[13]
$CuInSe_2$	199	207	[30]	135	—	
$AgGaS_2$	318	325	[13]	132	157	[13]
$AgGaSe_2$	225	208	[10]	120	133	[10]
$AgGaTe_2$	186	200	[28]	110	115	[28]
$AgInSe_2$	190	200	[31]	109	106	[31]

Table 4
Comparison of calculated and experimental frequencies (in cm^{-1}) of the A_1, B_1^1 and B_1^2 modes

Compound	$\bar{\nu}(A_1)$ calc.	exp.	Ref.	$\bar{\nu}(B_1^1)$ calc.	exp.	Ref.	$\bar{\nu}(B_1^2)$ calc.	exp.	Ref.
$CuAlS_2$	318	316	[13]	486	443	[13]	238	269	[13]
$CuGaS_2$	310	312	[26]	382	243	[33]	204	203	[13, 33]
					358	[13]		238	[26]
					401	[26]			
$CuGaSe_2$	177	187	[34]	270	—	—	176	—	
$CuInS_2$	293	294	[13]	342	—		175	167	[35]
$AgGaS_2$	302	295	[13]	373	224	[6]	163	160	[6]
					334	[5, 13]		179	[33]
								190	[13]
$AgGaSe_2$	176	179	[33]	266	—		147	—	

Considering the results for the B_1 modes we see that only in the case of the B_1^2 modes of $CuGaS_2$, $CuInS_2$ and $AgGaS_2$ there are experimental frequency values which agree with the theoretical ones (Table 4). In the case of the B_1^1 modes the experimental frequency values differ largely from author to author (see, for instance, the results for $CuGaS_2$), and in no case an approximate agreement between theory and experiment could be found. Obviously, it must be concluded that all the frequencies reported are not related to the B_1^1 modes. In this connection it is interesting to note that the calculated values for the B_1^1 mode frequencies are always very close to the frequencies of the longitudinal E^1 and B_2^1 modes [4, 10, 13, 26, 27]. Thus, it cannot be excluded that the B_1^1 modes are always masked by the E_{LO}^1 and $B_{2\mathrm{LO}}^1$ modes which are both characterized by large scattering efficiencies in Raman measurements [5, 6].

Finally, it was of interest to look for the dependence of the force constants α_A and α_B on the bond length. In the sphalerite-structure binary compounds it has been found that the bond-stretching force constants approximately follow the relation $\alpha = A\ d^{-3}$ [20, 21]. Furthermore, it has been established that in the copper halides also crystallizing in the sphalerite structure the force constants are reduced in dependence on the degree of p–d hybridization of the valence band [21]. Because of the strong admixture of Cu $3d$ and Ag $4d$ states to the chalcogen p states in the $A^{I}B^{III}C_2^{VI}$ compound valence bands ([35] and references therein) similar effects are expected in these compounds, too. Figure 2 shows a double-logarithmic plot of the force constants from Tables 1 and 2 against the bond lengths taken from [17]. In complete analogy to the situation in the $A^{III}B^{V}$ and $A^{II}B^{VI}$ compounds we find that the α_B values of all compounds can be described by a single function of the type $\alpha_B = A_B\, d_B^{-n}$. A least-squares fit of the data points yields $n = 3.01$ in accordance with the value found in the binary compounds. For the force constant α_A we have two different curves for the $CuB^{III}C_2^{VI}$ and $AgB^{III}C_2^{VI}$ compounds, respectively, which are both below the curve for α_B. The result that at the same bond length d_A the force constant for a silver compound is larger than the force constant for a copper compound (see Fig. 2) is in agreement with the well established experimental fact that the admixture of the noble metal d states to the uppermost valence is larger in the copper compounds than in the silver compounds [18]. It can be seen from Fig. 2 that the slope of the α_A curves is practically the same as that of the α_B curve. This means that the degree of the

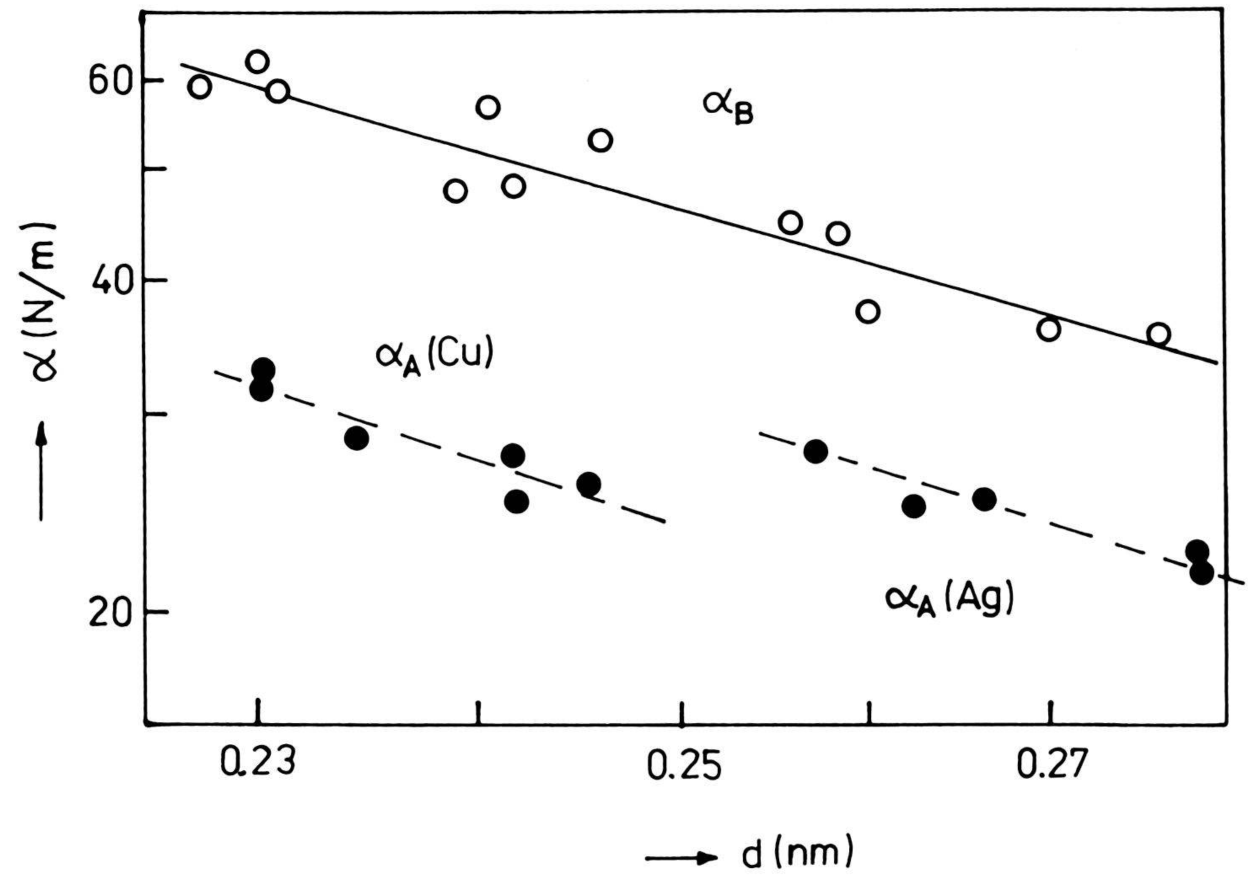

Figure 2
Double-logarithmic plot of the force constants α_A and α_B against the bond length

partial dehybridization of the sp^3 orbitals due to the noble metal *d* electrons which is responsible for the weakening of the bond [21] remains nearly constant in both compound groups.

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