Tab. 3. IR-Absorptionsmaxima des β-In_2S_3 und des $CdIn_2S_4$ (cm^{-1}).

β-In_2S_3			$CdIn_2S_4$[4]		
359	m-s				
336	s	sh			
325	vs	b			
311	vs		311	vs-s	
291	m				
267	s	sh			
260	s				
234	vs	b	231	vs	b
216	s				
194	m	sh			
168	m		170	s	sh b
156	w	sp			
94	w	sp			
54	vw		68	m	

vs = sehr stark, s = stark, m = mittel, w = schwach, vw = sehr schwach, b = breit, sh = Schulter, sp = scharf.

Entsprechend der großen Zahl von IR-aktiven Spezies zeigt das Absorptionsspektrum des β-Indiumsulfids im langwelligen Infrarot ($35-500\,cm^{-1}$) einen verhältnismäßig komplizierten Aufbau (vgl. Abb. 2). Eine zweifelsfreie Zuordnung der einzelnen Maxima (vgl. Tabelle 3) zu den entsprechenden Schwingungsformen war nicht möglich. Wir beabsichtigen daher, Einkristalluntersuchungen zur experimentellen Unterscheidung der Schwingungen der Typen A_{2u} und E_u durchzuführen.

Experimentelles: Die Darstellung des β-Indiumsulfids erfolgte nach KLEMM und VOGEL [11] durch mehrstündiges Überleiten von H_2S über In_2O_3 bei 500 bis 700 °C, beziehungsweise durch Zusammenschmelzen der Elemente bei 600 °C [5]. Die IR-Spektren wurden in Nujol mit den Gitterspektrographen Beckman IR 11 und Perkin Elmer 225 aufgenommen.

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A Semiempirical-Wolfsberg-Helmholtz-Crystal Field Approach to the Crystalline State (CaS, SrS)

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The aim of this work is to introduce a semiempirical method that can be used to describe the crystalline state. For this purpose we used two methods (Wolfsberg-Helmholtz and Crystal field) combined together and applied these to evaluate (among other quantities) the charges in CaS and SrS.

Method of calculation

CaS and SrS have a NaCl structure. The calculation was based on the following assumptions: the crystals can be divided into clusters in which each calcium (strontium) atom is surrounded by six neighbour sulphur atoms. This can be justified by the fact that the distance between the calcium (strontium) atom and the sulphur atom in the isolated cluster is smaller than the distance between the respective atoms belonging to different clusters.

The Hamiltonian which is appropriate to the problem is

$$H = H_0 + V_c\,,$$

where H_0 is the Hamiltonian describing one isolated cluster and V_c is the perturbing potential of all other clusters on the first one. H_0 was taken in the approximation of Wolfsberg-Helmholtz and V_c is given by:

$$V_c = \sum_{i,j} \frac{Z_{\text{eff}}}{r_{ij}}$$

where Z_{eff} are effective charges on atoms from neighbour clusters and r_{ij} are distances between these atoms and the i-th electron from the isolated cluster. The parametrization of the Wolfsberg-Helmholtz Hamiltonian was taken in a form proposed by BASCH et al. [1] with values from Ref. [1] for calcium and sulphur, and from Ref. [2] for strontium. In the last case some rough interpolation from Moor's table [3] was necessary. The calculation was carried out to self consistency for all charges Z_{eff} on atoms from all clusters. The population analysis was calculated in a standard manner [4]. The quantities that are interesting from the chemist's point of view are the charges on calcium, strontium and sulphur.

The calculated values are 0.43 for calcium and 0.37 for strontium in the respective sulphides. On the basis of Pauling's electronegativities the bonds of the studied crystals should have a predominantly ionic character, with a large static ionic charge. Our results give a lower ionic charge than that predicted by electronegativity. A lower ionic charge is suggested also by the FIR spectra of CaS and SrS [5].

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