

# MANIFESTATION OF CRYSTAL STRUCTURE SINGULARITIES IN THE IR SPECTRA OF GERMANIUM DICHALCOGENIDES

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We report the first investigations of the spectra of  $\text{GeS}_2$  and  $\text{GeSe}_2$  in the far infrared, where we observed, in addition to the ordinary vibrational bands, also absorption bands similar to those seen in the spectra of molecular crystals.

One of the direct methods of studying the structure of a substance is to analyze its IR spectrum in the region where the crystal lattice absorption bands are located. To interpret the results, however, it is necessary to study as large a number of IR spectra of similar compounds as possible. Such compounds are the families of the mono- and dichalcogenides of germanium.

We have investigated, for the first time, the IR spectra of powders of crystals of these compounds in the region from  $700$  to  $33 \text{ cm}^{-1}$ , where their vibrational absorption spectra are located. The crystals were grown in quartz ampules from melts of suitable batches of Ge with S or Se. The spectra were studied with the UR-10 and FIS-3 analyzers. The crystal powders were pressed in hot polyethylene.

According to their x-ray structure analysis, GeS and GeSe are isostructural and crystallize in a rhombic lattice of space group  $D_{2h}^{16}$  - Pcmn [1]. In such a structure, the valently bound atoms of different kinds form double layers, and each atom is surrounded by neighbors of the other kind forming a strongly distorted octahedron. In "their own" double layer, the Ge atoms have three nearest and two more remote neighbors; the farthest neighbor lies in the next layer. The bonds between atoms of different sorts inside the double layer have an ion-covalent character, whereas the bond between neighboring layers is greatly weakened.

The IR transmission spectra of GeS and GeSe (Fig. 1) have a complicated absorption band and are practically identical in form, although in GeSe the entire band is regularly shifted to the long-wave region of the spectrum. Since this shift is due to the replacement of the S atom in the lattice by the heavier Se, it can be assumed that the monochalcogenides of germanium are indeed isostructural [1].

X-ray structure investigations of  $\text{GeS}_2$  and  $\text{GeSe}_2$  have shown that they crystallize in a rhombic lattice with space group  $D_{2h}^{13}$  - Pmmn, i.e., they are isostructural [2, 3]. Their structure is in fact a strongly deformed structure of the  $\text{CdI}_2$  type. The latter is made up of two-dimensional platelets of octahedral groups of  $\text{CdI}_6$ , resulting in the formation of layers of the metal atoms (A), which produce the metric basis of the crystal lattice and are



Fig. 1. IR transmission spectra of germanium monochalcogenides: 1 - GeS, 2 - GeSe.

arranged between layers of atoms of the other kind, i.e., the layer arrangement is -B-A-B-B-A-B-. A characteristic feature of this structure, besides its layered character, is that the interatomic distances in the lattice are decreased to values smaller than the covalent radii of the atoms. For example, in  $\text{GeS}_2$  the interatomic Ge-S distances range from 2.07 to 2.19 Å whereas the sum of the covalent radii of these atoms is 2.25 Å [4]; a similar picture is observed in  $\text{CdI}_2$ ,  $\text{GeSe}_2$ , etc.

The IR transmission spectra  $\text{GeS}_2$  and  $\text{GeSe}_2$  (Fig. 2) have no analogs in the spectra of the various classes of inorganic crystals investigated to date. In addition to the usual vibrational rather broad absorption bands, which differ in intensity, they contain a number of intense bands with half-width on the order of 5 - 7  $\text{cm}^{-1}$ , which are characteristic of molecular crystals. These bands appear in the IR spectra of  $\text{GeS}_2$  and  $\text{GeSe}_2$ , respectively, in the ranges from 190 to 100  $\text{cm}^{-1}$  and from 125 to 65  $\text{cm}^{-1}$ . These bands are not caused by the pressing of the powders of these crystals into a matrix, since a similar IR spectrum was obtained from the same powders placed between thin silicon plates. Evidently the molecular-type bands are a characteristic feature of the IR spectra of crystals having the peculiar layered structure of the  $\text{CdI}_2$  lattice.

Bonds that lead to the appearance of absorption bands of the molecular type can be realized between the chalcogen atoms and the double layers made up of them in the  $\text{GeS}_2$  and  $\text{GeSe}_2$  lattices. It must be emphasized that the bonds that become established in the double two-dimensional layers of the chalcogen atoms differ in character from the bonds realized between them in three-dimensional lattices of crystals of these substances, since the spectrum of the latter lies in the region of shorter wavelengths, and contains no vibrational bands with small half-widths.

The disposition (and bonds) of the chalcogen atoms in the double layers of the  $\text{GeS}_2$  and  $\text{GeSe}_2$  lattices is apparently governed by the Ge atoms that make up the basis of the lattice, and does not duplicate the disposition (and bonds) of the chalcogen atoms in the crystals proper. This is confirmed by the IR spectrum of  $\text{GeS}_2$  and  $\text{GeSe}_2$  obtained at 170°C, in which the molecular-type bands experience no changes whatever, although this temperature is higher than the melting temperature of sulfur (112.8°C).

The complex vibrational absorption bands that appear in the IR spectra of  $\text{GeS}_2$  and  $\text{GeSe}_2$  at shorter wavelengths than those of the molecular bands can be regarded as similar if account is taken of another feature of these spectra, namely the presence in them of a band of identical shape with maximum at 338  $\text{cm}^{-1}$ , observed in  $\text{GeS}_2$  on the right of the most intense absorption bands, and in  $\text{GeSe}_2$  on the left, i.e., it is not shifted when the chalcogen atoms are interchanged. Since the position of this band coincides with the position of the absorption band of crystalline Ge, and the Ge-Ge bonds form in the germanium dichalcogenides the basis of the crystal lattice, this band is apparently due to vibrations of Ge-Ge atom pairs. In this case, interchange of the chalcogen

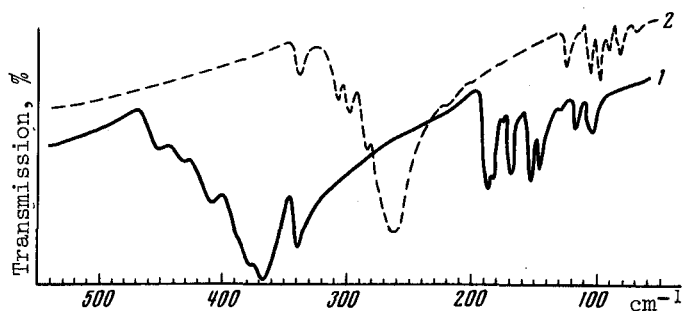


Fig. 2. IR transmission spectra of germanium dichalcogenides: 1 -  $\text{GeS}_2$ , 2 -  $\text{GeSe}_2$ .

atoms does indeed not cause a shift of the absorption band in the spectra. The exceptional similarity between the details of the complex IR spectra of the germanium dichalcogenides indicates that their crystals are isostructural [2, 3].

The spectra of the mono- and dichalcogenides of germanium differ substantially both in form and in the position of the most intense vibrational absorption bands. For example, in GeS these bands lie in the range from 285 to 235  $\text{cm}^{-1}$ , whereas the main band of  $\text{GeS}_2$  lies in the region of 370  $\text{cm}^{-1}$ . At the same time, an appreciable change takes place in the mean interatomic distances, from 2.58 Å for GeS to 2.15 Å for  $\text{GeS}_2$ . This indicates a change in the character and in the binding forces between the  $\text{S}^{2-}$  and  $\text{Ge}^{2+}$  or  $\text{Ge}^{4+}$  ions. In particular [5], the IR spectra of amorphous films evaporated from crystalline GeS possesses only a band with maximum at 370  $\text{cm}^{-1}$ , which is produced when there are bonds between the  $\text{S}^{2-}$  and  $\text{Ge}^{4+}$  ions; this band is transformed into the complex band of GeS only after the film becomes crystallized. However, when amorphous films are evaporated from  $\text{GeS}_2$  and  $\text{GeSe}_2$  crystals, the characteristic and most intense band of these compounds appears immediately. The  $\text{Ge}^{4+}$  ion apparently plays a special role in the formation of the crystal structures of germanium chalcogenides. This is evidenced, in particular, by the coincidence of the positions of the weak high-frequency absorption bands of GeS and GeSe with the positions of the most intense bands in the spectra of  $\text{GeS}_2$  and  $\text{GeSe}_2$ .

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#### \* CYCLOTRON RESONANCE ON NON-EXTREMAL ORBITS

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A new phenomenon - cyclotron resonance on non-extremal orbits - was observed at the limit of the cyclotron-frequency spectrum. This limit was produced artificially by adjusting the sample thickness to cut off the orbits of electrons belonging to Fermi-surface thicknesses larger than a certain limit. The phenomenon, observed in bismuth at  $\sim 9$  GHz and 0.35°K, uncovers a possibility of investigating the properties of electrons belonging to non-extremal sections of the Fermi surface.

All methods used to investigate the dynamics of definite groups of metal conduction electrons, based on the use of cyclotron resonance (CR), quantum oscillations, size effects, etc., yield information only on the electrons belonging to extremal sections of the Fermi surface (FS). In the case of a convex FS (Fig. 1a), these are the central section and the limiting point, corresponding to the extremal values of the effective mass  $m^*$  and of the cyclotron frequency  $\Omega = eH/m^*c$  (Fig. 1b). The only known possibility, in principle, of investigating the properties of electrons belonging to intermediate sections of the FS is to use quantum CR [1], which should occur at the discrete intermediate frequencies that result from the breakup by the  $\Omega(p_y)$  spectrum of the Landau