

## Lattice Vibration Spectra. XXVI.

### Far-Infrared Spectra of the Ternary Skutterudites $\text{CoP}_{3-x}\text{As}_x$ , $\text{CoAs}_{3-x}\text{Sb}_x$ , and $M\text{Ge}_{1.5}\text{Y}_{1.5}$ ( $M = \text{Co, Rh, Ir}$ ; $Y = \text{S, Se}$ )

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The infrared spectra of the skutterudite solid solutions  $\text{CoP}_{3-x}\text{As}_x$  and  $\text{CoAs}_{3-x}\text{Sb}_x$  and the ordered ternary skutterudites  $M\text{Ge}_{1.5}\text{Y}_{1.5}$  ( $M = \text{Co, Rh, Ir}$ ;  $Y = \text{S, Se}$ ) have been studied. In the system  $\text{CoP}_{3-x}\text{As}_x$  a complete mixed-crystal series has been obtained. In the system  $\text{CoAs}_{3-x}\text{Sb}_x$  a miscibility gap has been found. The infrared spectra of the mixed crystals are influenced by large plasmon-phonon interactions with anomalous temperature shifts of the resonance frequencies. Substitution of arsenic in  $\text{CoAs}_3$  by small amounts of phosphorus or antimony results in an additional short-waved mode at 362 and 342  $\text{cm}^{-1}$ , respectively, which can be assigned to an internal vibration of the four-membered anionic rings not allowed in the binary skutterudites. The infrared spectra of the ordered ternary skutterudites  $M\text{Ge}_{1.5}\text{Y}_{1.5}$  ( $M = \text{Co, Rh, Ir}$ ) show a large number of the total of 64 ir allowed lattice modes, whereas the spectra of the rhodium compounds are mainly of the free carrier type.  $\text{RhGe}_{1.5}\text{S}_{1.5}$  and the firstly obtained  $\text{RhGe}_{1.5}\text{Se}_{1.5}$  exhibit small deviations from the formerly claimed pseudo-cubic cell. The lattice constants (space group  $R\bar{3}$ ) are  $a = 828.2(1)$  pm,  $\alpha = 89.85(1)^\circ$  and  $a = 854.6(1)$  pm,  $\alpha = 89.86(1)^\circ$ , respectively.

## Introduction

In recent studies we have found that the far-infrared spectra of the binary skutterudites  $\text{MX}_3$  ( $M = \text{Co, Rh, Ir}$ ,  $X = \text{P, As, Sb}$ ) are influenced by both free-carrier and optical-phonon contributions (1). In the case of the semiconducting material  $\text{CoP}_3$  we found strong plasmon-phonon coupling with large anomalous temperature shifts of the ir absorption and reflection frequencies. On the other hand, the free-carrier contribution to the spectra of  $\text{CoAs}_3$  and  $\text{CoSb}_3$ , which are likewise semiconducting materials, is only small and, hence, the spectra of these compounds are of pure lattice vibration type.

In the meantime we were successful in preparing solid solutions of the cobalt skut-

terudites, viz., the series  $\text{CoP}_{3-x}\text{As}_x$  and  $\text{CoAs}_{3-x}\text{Sb}_x$ , and we intended to study the very different spectroscopic properties of the binary compounds using the obtained mixed crystals as intermediates. As examples of skutterudites with a superstructure ordering in the nonmetal lattice we investigated the ternary compounds  $M\text{Ge}_{1.5}\text{Y}_{1.5}$  ( $M = \text{Co, Rh, Ir}$ ;  $Y = \text{S, Se}$ ), recently found by Korenstein *et al.* (2) and Lyons *et al.* (3), see Fig. 1.

## Mixed Crystal Series $\text{CoP}_{3-x}\text{As}_x$ and $\text{CoAs}_{3-x}\text{Sb}_x$

The skutterudites  $\text{CoP}_3$  and  $\text{CoAs}_3$  have been found to form a complete series of solid solutions which obey Vegard's rule.

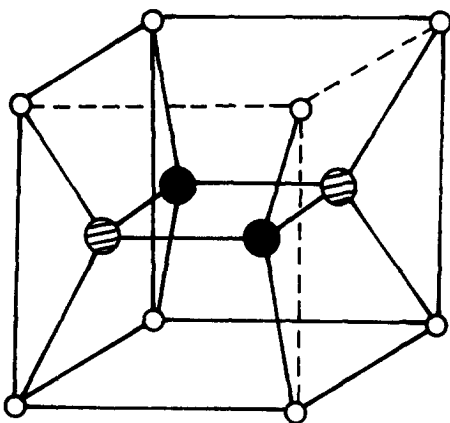


FIG. 1. Part of the crystal structure of the ordered skutterudite  $\text{CoGe}_{1.5}\text{S}_{1.5}$ . Ge and S are arranged in a four-membered ring. The metal atoms form a simple cubic lattice, see (3).

Thus the composition of the samples can be determined from the unit cell dimensions. In the series  $\text{CoAs}_{3-x}\text{Sb}_x$  we have found a miscibility gap in the region of  $x = 0.4$  to 2.8. The lattice constants of the two mixed crystals with the highest degree of substitution are 825.1(1) and 892.8(1) pm, respectively. The unit cell dimensions of the cubic binary phases have been found to be in agreement with the literature, 770.73(2) ( $\text{CoP}_3$ ) (4), 820.55(3) ( $\text{CoAs}_3$ ), and 903.47(6) pm ( $\text{CoSb}_3$ ) (5).

The far-infrared absorption spectra of some of the obtained  $\text{CoP}_{3-x}\text{As}_x$  and  $\text{CoAs}_{3-x}\text{Sb}_x$  solid solutions are shown in Figs. 2 and 3. Three features of the spectra are remarkable.

(i) The substitution of small amounts of arsenic by both phosphorus and antimony results in an additional short-waved mode at  $362\text{ cm}^{-1}$  ( $\text{CoP}_{0.25}\text{As}_{2.75}$ ) and  $342\text{ cm}^{-1}$  ( $\text{CoAs}_{2.9}\text{Sb}_{0.1}$ ), respectively. The highest wavenumbered lattice mode of  $\text{CoAs}_3$  itself is  $330\text{ cm}^{-1}$  (see Fig. 2). The intensity of the additional modes rapidly increases with increasing content of phosphorus or antimony in the alloy. The appearance of a short-waved mode also in the case of the antimony doped cobalt arsenide excludes

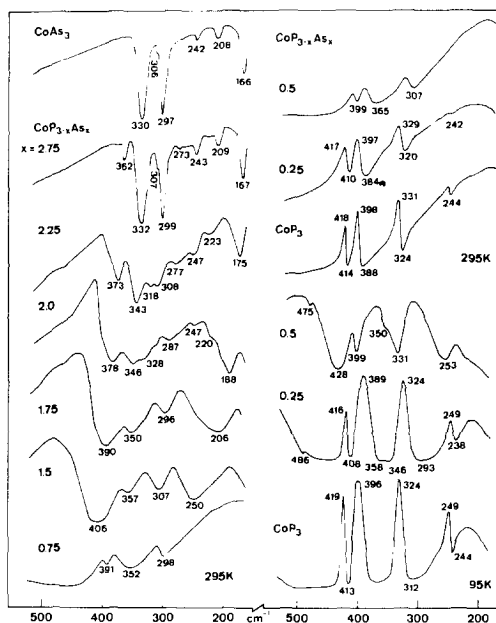


FIG. 2. Infrared absorption spectra of some mixed crystals  $\text{CoP}_{3-x}\text{As}_x$  (CsI, PE 580) at 295 and 95 K.

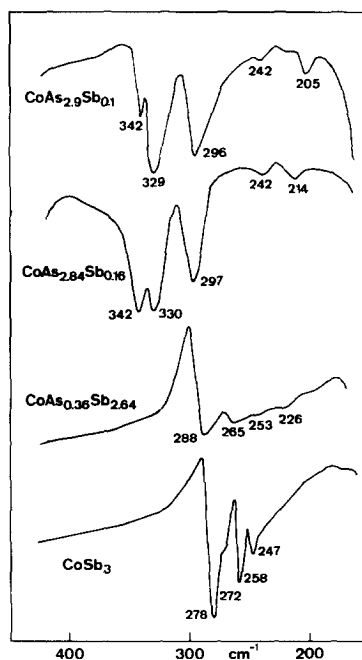


FIG. 3. Infrared absorption spectra of some mixed crystals  $\text{CoAs}_{3-x}\text{Sb}_x$  (CsI, PE 580), see also Fig. 4.

the possible explanation that the new modes are due to an ordinary two-mode behavior of the lattice vibrations. It is more probable that an ir disallowed internal vibration of the anionic  $X_4$  ring (see Fig. 1) becomes active in the solid solution. As, in the case of small anionic substitution, only monosubstituted  $X_4$  rings (besides nonsubstituted ones) are present in the skutterudite solid solutions, the observed additional modes must be assigned to the antisymmetric stretching vibrations of these planary  $PA_3$  and  $SbA_3$  units. In the case of cobalt antimonide doped with small amounts of arsenic no additional short-waved mode is observed in the ir spectrum. We assume that the corresponding stretching mode of the  $AsSb_3$  ring, which must be found at lower wavenumbers, is hidden under the very strong lattice vibrations of  $CoSb_3$  found in the range from 250 to 280  $cm^{-1}$  (see Fig. 3).

(ii) Both the X-ray investigations and the far-infrared spectra of the skutterudites  $CoP_{3-x}As_x$  exclude any superstructure ordering in the mixed crystals. Any other arrangements than a statistical distribution of  $X_4$ ,  $YX_3$ , *cis* and *trans*  $X_2Y_2$ ,  $XY_3$  and  $Y_4$  units would destroy the high symmetry of the skutterudite structure and greatly enlarge the number of the ir-allowed lattice modes. To what extent the translation symmetry of the skutterudite is destroyed in the solid solutions and whether the observed spectra are rather due to critical points in the Brillouin zones than to  $|\vec{q}| = 0$  lattice vibration modes, cannot be verified.

(iii) As is seen in Fig. 2 the substitution of arsenic by phosphorus results in an increasing free-carrier contribution to the spectra of the  $CoP_{3-x}As_x$  solid solutions. From Kramers-Kronig analysis of the reflection spectra we determined the plasma frequency of the free carriers to be 103  $cm^{-1}$ , and 820  $cm^{-1}$  for our samples of binary  $CoAs_3$  and  $CoP_3$  (6). The plasma frequency of the  $CoP_{3-x}As_x$  mixed crystals

continuously varies within this region and overlaps the lattice vibration modes step by step. From this behavior a large plasmon-phonon interaction results in both the  $CoP_{3-x}As_x$  mixed crystals and in the binary  $CoP_3$ .

This is also shown by the rather anomalous temperature shift of the frequencies of the lattice modes (see Fig. 4). Going from low temperature to ambient temperature the usual softening of the lattice vibration modes due to the thermal expansion of the lattice is observed ( $d\bar{\nu}/dT < 0$ ). But at higher temperatures, i.e., higher concentrations of free carriers, the absorption bands are shifted back to higher wavenumbers with increasing temperature ( $d\bar{\nu}/dT > 0$ ). The latter behavior is caused by plasmon-phonon interaction. This can be realized from oscillator model calculations using three contributions to the dielectric constant

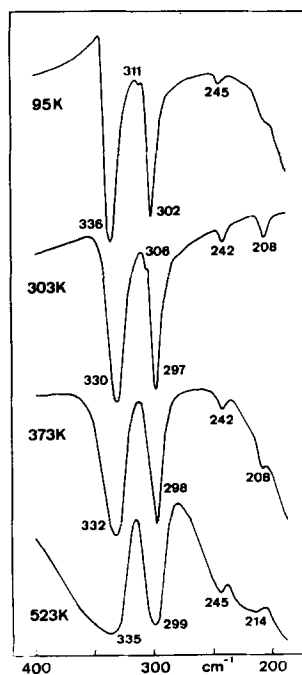


FIG. 4. Infrared absorption spectra of  $CoAs_3$  at different temperatures (CsI, PE 580).

$$\hat{\epsilon} = \hat{\epsilon}_{\infty} + \hat{\epsilon}_1 + \hat{\epsilon}_{fc}$$

( $\hat{\epsilon}_{\infty}$  = electronic,  $\hat{\epsilon}_1$  = lattice vibration, and  $\hat{\epsilon}_{fc}$  = free-carrier contribution) (7, 8).

### Ternary Skutterudites of $\text{CoGe}_{1.5}\text{S}_{1.5}$ type

In addition to the ordered skutterudites  $\text{CoGe}_{1.5}\text{S}_{1.5}$ ,  $\text{CoGe}_{1.5}\text{Se}_{1.5}$ ,  $\text{RhGe}_{1.5}\text{S}_{1.5}$ ,  $\text{IrGe}_{1.5}\text{S}_{1.5}$ , and  $\text{IrGe}_{1.5}\text{Se}_{1.5}$  described in the literature (2, 3), we obtained a new compound of this type,  $\text{RhGe}_{1.5}\text{Se}_{1.5}$ . The X-ray pattern of this compound shows characteristic splittings of the reflexes of the pseudocubic ordered skutterudites (space group  $R3$ ,  $\alpha = 90^\circ$ ). Indexing of the observed pattern confirmed the rhombohedral space group proposed by Korenstein *et al.* (2), but with  $\alpha \neq 90^\circ$ . Guinier photographs indicate that the rhombohedral angle of  $\text{RhGe}_{1.5}\text{S}_{1.5}$  also deviates from  $90^\circ$ . The unit cell dimensions of  $\text{RhGe}_{1.5}\text{S}_{1.5}$  and  $\text{RhGe}_{1.5}\text{Se}_{1.5}$  have been found to be  $a = 828.2(1)$  pm,  $\alpha = 89.85(1)^\circ$  and  $a = 854.6(1)$  pm,  $\alpha = 89.86(1)^\circ$ , respectively.

The obtained ir spectra of the ternary skutterudites  $\text{CoGe}_{1.5}\text{S}_{1.5}$ ,  $\text{CoGe}_{1.5}\text{Se}_{1.5}$ ,  $\text{IrGe}_{1.5}\text{S}_{1.5}$ , and  $\text{IrGe}_{1.5}\text{Se}_{1.5}$  are given in Fig. 5. The large number of lattice vibration modes in the spectra of these compounds demonstrates the ordering in the nonmetal lattice and, hence, the lowering of the cubic symmetry of the skutterudites, and so supports the X-ray results. Unit cell group analysis on the basis of space group  $R3$  (unit cell group  $C_3$ ) predicts

$$\Gamma = 32A + 32E,$$

i.e., 64 ir- and Raman-allowed modes. From the point symmetry of a planar ( $C_{2h}$ ) *trans*- $X_2Y_2$  molecule,

$$\Gamma = 3A_g + 1A_u + 2B_u,$$

3 ir-active internal vibrations are predicted.

It is remarkable that substitution of cobalt by iridium does not cause a long-waved shift of the observed absorption bands,

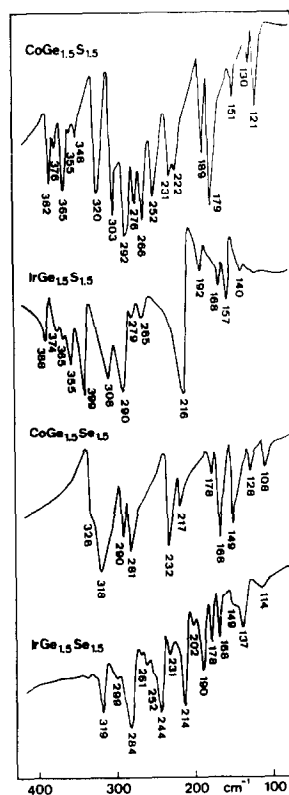


FIG. 5. Infrared absorption spectra of  $\text{CoGe}_{1.5}\text{S}_{1.5}$ ,  $\text{IrGe}_{1.5}\text{S}_{1.5}$ ,  $\text{CoGe}_{1.5}\text{Se}_{1.5}$ , and  $\text{IrGe}_{1.5}\text{Se}_{1.5}$  (Nujol, Bruker IFS 114).

especially in the case of the short-waved ones, whereas the substitution of sulfur by selenium results in the expected shifts to lower wavenumbers. From these spectral features it can be concluded that the short-waved modes are mainly internal ones. On the other hand, there is an additional indication that the short-range forces in chalcogenides and pnictides of  $5d$  transition metals are much stronger than those of  $3d$  metals, see also (9).

The ir spectra of the mixed rhodium skutterudites only show a very broad absorption band in the whole spectral region from  $\approx 1000$  to  $50$   $\text{cm}^{-1}$ . This is due to higher free-electron concentrations in these compounds. Even at liquid nitrogen temperatures it was not possible to record the pure lattice vibration spectra (7).

## Experimental

$\text{CoP}_{3-x}\text{As}_x$ ,  $\text{CoAs}_{3-x}\text{Sb}_x$ , and  $M\text{Ge}_{1.5}\text{Y}_{1.5}$  ( $M = \text{Co}, \text{Rh}, \text{Ir}$ ;  $Y = \text{S}, \text{Se}$ ) were prepared by heating stoichiometric mixtures of the elements in closed silica tubes at  $600^\circ\text{C}$  for 14 days and quenching in ice water. X-Ray analysis was performed with Guinier powder photographs, using  $\text{CuK}\alpha_1$  radiation and  $\text{SiO}_2$  as internal standard. Unit cell dimensions have been refined by least-squares method.

The infrared absorption spectra were recorded in the range from  $4000$  to  $180\text{ cm}^{-1}$  on the Perkin-Elmer model 580 grating spectrophotometer (CsI-technique) and in the range from  $700$  to  $40\text{ cm}^{-1}$  on the Bruker model IFS 114 Fourier-transform interferometer (Nujol mulls). A variable temperature cell (RIIC VLT 2) was used for the low- and high-temperature measurements.

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