FIG. 2. Spectra for the E1 and A1 polariton at various scattering angles.

changing the diameter of the iris and circular diaphragm or altering the imaging ratio. Then only two different lens systems are necessary to cover the range $0 < \varphi < 8^\circ$.

The experiments were carried out with a Spex 1402 double grating monochromator and an argon laser with an output of 1 W at 514.5 nm. The laser beam was focussed on the sample with a lens of long focal length. A lens combination of $f_s = 15$ cm and $f_c = 30$ cm was chosen for small scattering angles ($< 2^\circ$) and $f_s = 10$ cm and $f_c = 20$ cm for larger ones. For an illustration we give the figures of the distances and aperture used with the first system. The total focal length in the horizontal plane is $f_{\text{tot}} = 10$ cm and remains f_s for the vertical plane. For an object distance $b = 30$ cm and a diameter of 12 mm for the annular system an angle $\varphi = 1.2^\circ$ results for the light cone. Because of a refractive index of 2 for ZnO the scattering angle becomes 0.6° . A crystal length $L = 5$ mm gives a thickness $G = 50 \mu$ and represents the minimum slit width of the monochromator, because of an imaging ratio of 1:2. On the other hand, G gives the minimum annular aperture. However, the width of an annular aperture of only 50μ is difficult to align, therefore we worked with one of about 0.5 mm and accepted an uncertainty of about 10% for the scattering angle.

We have measured the dispersion branches of the E1 and A1 polariton in ZnO with the optical setups described above. In addition we placed a slit diaphragm behind the lens system, because ZnO is an uniaxial crystal and therefore scatters differently in different planes. The left part of Fig. 2 shows spectra for several scattering angles in the case of the $x(yz)x$ configuration. The E1 polariton shifts from about 380 cm^{-1} for larger scattering angles to 110 cm^{-1} for $\varphi' = 0.36^\circ$ and confirms the results of Porto *et al.*³ The half width of the polariton line of the present work is reduced by a factor of about 2 and therefore a lower limit of 0.36° for the scattering angle has been reached. In the $x(zz)x$ configuration, where the E1 polariton shifts only slightly and remains well separated from the laser line our lower limit was 0.28° . The right part of Fig. 2 shows spectra for the A1 polariton. Here again the lowest scattering angle is defined by the onset of an overlap of polariton line and exciting laser line. A more detailed discussion of the dispersion of the A1 polariton is given in Ref. 4.

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High Pressure and Temperature Infrared Gas Cells

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Index Headings: Infrared instrumentation; High pressure gas cell; High temperature gas cell.

In the literature the construction of some high pressure infrared gas cells has been described.^{1,2} However, these cells show, just as the commercially available high pressure gas cells, many problems with the cell windows. For our research on infrared integrated intensities we needed reliable pressure cells, which could be used at pressures up to 90 atm and at temperatures up to 150°C . As reliable cells fulfilling both conditions simultaneously can practically not be made, two cells were designed, one with maximum operating conditions: 90 atm at 50°C ; the other, 150°C at 20 atm. Besides, attention was given to the additional requirements of large window aperture and optical path length. Recent developments in the construction of window sealings for high pressure infrared liquid cells³⁻⁶ were successfully applied to the construction of the gas cells.

All parts of the cell body and the end caps of both cells are made of stainless steel 316. The heating cover of the high temperature cell is made of brass. KBr is used as window material, but CsBr windows will be mounted in the high pressure gas cell in the near future, in view of at one hand the better mechanical properties⁷ and at the other hand the useful gain in wavelength range. The following sealing materials are used: viton O-rings, flat Teflon rings, flat silicon rubber rings, and nylon packing support rings. In both cells, thin spacers of kapton 500 film (polyimide film coated with Teflon) are placed between the windows and the cell body as well as between the windows and the end caps.

A cross-section of the high pressure gas cell is given in

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FIG. 1. The high pressure gas cell. 1, cell body; 2, O-ring; 3, end cap; 4, window; 5, packing press ring; 6, packing support ring; 7, Teflon packing ring; 8, silicon rubber packing ring; 9 and 10, spacers; 11, opening for inlet tube; 12, thermocouple hole.

FIG. 2. The high temperature gas cell. 1, cell body; 2, heating cover; 3, heating element; 4, opening for inlet valve; 5, end cap; 6, window; 7 and 8, O-rings; 9 and 10, spacers. Not shown in the figure: thermocouple hole, situated in the middle of the cell, between the inlet valves.

Fig. 1. The numbers in parentheses in the following description refer to Fig. 1.

The cell consists of three parts which can be screwed together; then the optical path length counts 135 mm. When the middle part is left out (as in Fig. 1), the optical path length decreases to 65 mm. The outer diameter of the cell body (1) is 50 mm and the total length is 190 or 120 mm, respectively. The end caps (3) are screwed on the cell body and have a slightly conical opening with the smaller diameter being 20 mm. The cell body has an inner diameter of 20 mm, while the windows (4) have a diameter of 30 mm and a thickness of 20 mm. The window seal consists of flat rings with an outer diameter of 40 mm, an inner diameter of 30 mm and a thickness of 1 mm for the middle three Teflon rings (7) and 2 mm for the four silicon rubber rings (8). The outer Teflon rings fit against the three supporting

nylon rings (6). The remaining space between the seal and the end cap is filled up with a nylon press ring (5). The window packing fits with an inner and outer clearance of 0.01 mm, thus allowing the soft silicon rubber to flow by compression of the packing. The thin kapton spacers (9, 10) have a thickness of 0.125 mm. The sealing between the parts of the cell body is provided for by viton O-rings (2). Two inlet tubes (11) have been mounted on the cell. The temperature of the cell body can be measured by putting a thermocouple in the small hole (12). When pressurized with hydrogen, no pressure drop is observed in the cell after a few days operating at 90 atm and 50°C.

Fig. 2 shows a cross-section of the high temperature gas cell. In the following description the numbers in parentheses refer to Fig. 2.

A heating cover (2) with heating element (3) is

mounted around the cell body (1). The external cell dimensions are: length 120 mm; diameter 60 mm. The inner cell diameter is 20 mm and the optical path length counts 90 mm. The end caps (5) are screwed in the cell body and have a slightly conical opening with the smaller diameter being 20 mm. The windows (6) have a diameter of 30 mm and a thickness of 10 mm. Two viton O-rings (7, 8) provide for the sealing of the windows and end caps. The thin kapton spacers on both sides of the windows (9, 10) have a thickness of 0.125 mm. Two inlet valves (4) have been mounted on the cell, one for gases and one for liquids. The latter, with a minimum dead space, can be connected with the high pressure line in order to blow all the injected liquid into the cell.

After several hours operation at 150°C and a hydrogen pressure of 20 atm no leaks are observed.

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The Use of KBr Pressed Pellets in Inorganic Electronic Spectroscopy

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The practice of obtaining the infrared spectra of compounds pressed into a KBr matrix is a routine procedure in many chemical laboratories.¹ Recently we² and others³ have found that this technique is convenient for obtaining the near-infrared (4 000 to 13 000 cm^{-1}) and visible (13 000 to 25 000 cm^{-1}) electronic absorption spectra of coordination compounds. Because this method is apparently quite useful and may be of general interest to inorganic and solid-state chemists, we decided to investigate some of its qualitative and quantitative features.

In the past, the electronic absorption spectra of insoluble compounds have been obtained by mulling the sample with a suitable transparent oil or grease. This method suffers from both its lack of quantitivity and the

difficulty in reproducing sample particle size. Because both absorption and scattering are present in spectra obtained by using the mull technique it is often difficult to compare results from different laboratories. In addition, low temperature spectra are difficult to obtain with mulls because, when subjected to the high vacuum and low temperature necessary for such experiments the mulls tend to crack thereby leaving gaps in the sample.

We typically prepare KBr pellets by grinding approximately 200 mg of infrared quality KBr and then pressing this KBr under vacuum into a disc at approximately 20 000 lb/in². Fig. 1 shows the types of spectra typically observed for pure KBr pellets prepared in this manner. Fig. 1a illustrates the spectrum of a KBr pellet which is slightly fogged. This fogging of the pellet may arise from either adsorption of water on the pellet's surface or KBr which is not ground to a very fine powder. The linear increase of the relative absorbance of the pellet with increasing wavenumber is a consequence of the combined reflectance at the two surfaces of the pellet and the scattering within the pellet. It is possible to minimize the scattering of the pellet by using very finely ground KBr. The spectrum obtained in this way is shown in Fig. 1b. Such a pellet gives very little scattering from approximately 200 to 30 000 cm^{-1} . It is possible to balance the combined reflectivity and scattering shown in Fig. 1a by inserting an identical pellet in the reference beam of a double-beam spectrophotometer such as the Cary 14 which was used in this study. The result is the flat baseline shown in Fig. 1c. The use of a reference pellet increases the useful spectral range of the pellet to approximately 200 to 37 000 cm^{-1} . This spectral range covers the infrared and visible regions in which ligand-field transitions are observed. We have found that it is necessary to balance the additional scattering caused by a compound dispersed in the KBr pellet with the same weight of a transparent material dispersed in the reference KBr pellet. Ordinary granulated sugar serves this purpose very well and we have used it routinely in our work.

In order to check the quantitative usefulness of this

FIG. 1. a. The nir-VIS spectrum of a slightly fogged 0.6 mm thick KBr pellet vs air. b. The ir-VIS spectrum of a perfectly clear 0.6 mm thick KBr pellet vs air. c. The nir-VIS spectrum of the pellet in spectrum a vs an identical pellet.