PHYSICAL REVIEW VOLUME 105, NUMBER 1 JANUARY 1, 1957

Reflection Spectrum and Structure in the Exciton Absorption Peak of NaCl and KCl†

P. L. Hartman, J. R. Nelson, and J. G. Siegfried*
Department of Physics, Cornell University, Ithaca, New York

(Received September 17, 1956)

Measurements in the vacuum ultraviolet have been made on the transmission of thin films of NaCl and KCl and on the reflectivity of single crystals of these same salts. Comparison is made between the two types of measurements and with the absorptions measured in thin films by Schneider and O'Bryan. The agreement with the latter in the case of NaCl is good only over the region of the first absorption while in the case of KCl it is good over the whole region over which the measurements overlap. A new absorption is found in NaCl near 1100 A and in KCl just below 1000 A. In both salts the first fundamental absorption near 1600 A, presumed to be that of the exciton, as inferred from the reflectivity is at least a doublet at liquid nitrogen temperatures; but further multiplicity of the type predicted by Overhauser is not established, although possibly indicated. Absolute reflectivities of the order of 60% are measured at low temperatures.

A NUMBER of years ago work was started at Cornell on remeasuring the photoconductivity and photoemission done earlier on NaCl[1] with the hope of better correlating the phenomena with the optical behavior of the crystals.

The electrical measurements are still under way, but it seems appropriate to report on the methods used and the results obtained in the work on the optical behavior of NaCl and KCl, particularly in the region of their first fundamental absorption peaks. It has thus far been presented only at meetings.[2,3]

The curves usually referred to in the absorptions of NaCl and KCl (along with others of the alkali halides) are those of Hilsch and Pohl[4] as extended by Schneider and O'Bryan,[5] who also measured a variety of the alkali halides. The work of the latter was photographic, a comparison being made in the photographic densities recorded in a vacuum spectrograph of lines down to about 1100 A with and without the salt (evaporated on a LiF window, for which correction was made) in the path of the radiation. Their relative absorption measurements from salt to salt were only good to about 25%, but were thought to be fairly reliable in any one salt as a function of wavelength.

Since, in the present work, some desire was felt for making optical measurements on single crystals, ideally in which photoconductivity would then be measured, some method for investigating the single-crystal optical properties seemed necessary; it was clear that photoconductivity measurements in a thin evaporated film of uncertain constitution would be of questionable significance. However, the absorptions are so high that transmission measurements on single crystals are impossible.

In principle it is possible to predict for a material from its dispersion curve the positions of its absorption peaks. On the basis of such predictions for KCl and NaCl made by Herzfeld and Wolf[6,7] (giving for NaCl, absorptions at 342, 936, and 1543 A, and for KCl at 515, 975, and 1580 A), Pfund[8] reported a high reflectivity for these salts from cleavage surfaces at about 1547 and 1581 A, respectively. Subsequently Smith,[9] using a reflection method, observed these salts down to about 200 A, but his results are confusing and mostly unconfirmed.

The measurements here reported, for the most part, are based on the reflection method. The principal part of the apparatus consists of a vacuum monochromator working at close to normal incidence as indicated schematically in Fig. 1. The entrance slit is illuminated by and serves as part of the anode for a hydrogen capillary discharge as a source of radiation,[10] providing reasonable illumination from 1800 A to 900 A. The grating is of aluminum evaporated on glass, 15 000 lines to the inch and 1.5 m radius of curvature. The lamp is bolted directly on to the monochromator end plate and over the entrance slit, and also is displaced from the detection head of the apparatus, which is bolted

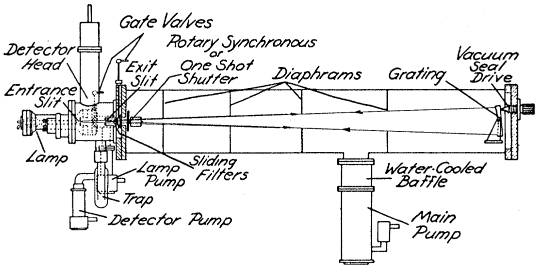

FIG. 1. Schematic diagram of the monochromator, lamp, and detector system. The cryostats in all cases are fitted into the extension up out of the detector head covering the exit slit. Gate valves allow closing off the monochromator. The shutter is Selsyn-operated.

---

† Research supported in part by the Office of Naval Research.

* Now with International Business Machines, Endicott, New York.

[1] J. N. Ferguson, Phys. Rev. **57**, 1089(A) (1940).

[2] Nelson, Siegfried, and Hartman, Phys. Rev. **99**, 658(A) (1955).

[3] P. L. Hartman, Phys. Rev. **99**, 1648 (1955).

[4] R. Hilsch and R. W. Pohl, Z. Physik **59**, 812 (1930).

[5] E. G. Schneider and H. M. O'Bryan, Phys. Rev. **51**, 293 (1937).

[6] K. F. Herzfeld and K. L. Wolf, Ann. Physik **78**, 35 (1925).

[7] K. F. Herzfeld and K. L. Wolf, *Handbuch der Physik* (Springer-Verlag, Berlin, 1928), Vol. 20, particularly Sec. II.

[8] A. H. Pfund, Phys. Rev. **32**, 39 (1928).

[9] A. Smith, Phys. Rev. **44**, 520 (1933).

[10] P. L. Hartman and J. R. Nelson, J. Opt. Soc. Am. (to be published).

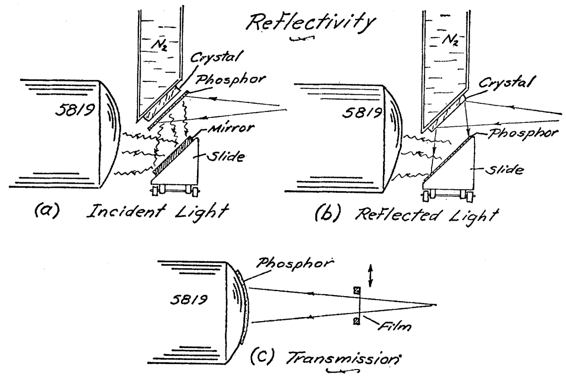

FIG. 2. Schematic arrangements for measuring reflectivity by getting the incident light in (a) and the reflected light in (b). Transmission is obtained by using (c) with the film in and out of the beam.

over the exit slit along side of the lamp also to the monochromator end plate. The two slits and a system of baffles provide for differential pumping between the lamp and the detection chamber, each unit being separately pumped. In a series of measurements above 1400 A carried out at liquid helium temperature, it was necessary to wax a thin window of LiF over the exit slit to prevent condensation of hydrogen on the sample being investigated. The exit and entrance slits were about 0.25 mm wide which make possible a resolution of about 4 A at the output. With a lamp pressure estimated at about a millimeter, the tank pressure is about 10^{-3} mm and the detector head about 5×10^{-5} mm when open to the system. With the LiF window in place the detector head pressure reaches about 10^{-6} mm when liquid air is used as a refrigerant in the detector head. The relative intensity of illumination is measured by means of an end-on photomultiplier monitoring the light given off by a sodium salycilate phosphor, which is irradiated by the uv light to be measured. This useful phosphor[11] was prepared by dissolving the salycilate in ethyl alcohol, adding an equal amount of ether, and then spraying this solution with an atomizer to form a thin layer on a suitable surface, either a front surface mirror, to increase the light collection of the multiplier, or on the end of the photomultiplier if it is used in line with the exit slit. The latter is a much more efficient way to use the phosphor, but in most of the work it was not feasible to do so. As used, the phosphor coating is translucent and diffuse.

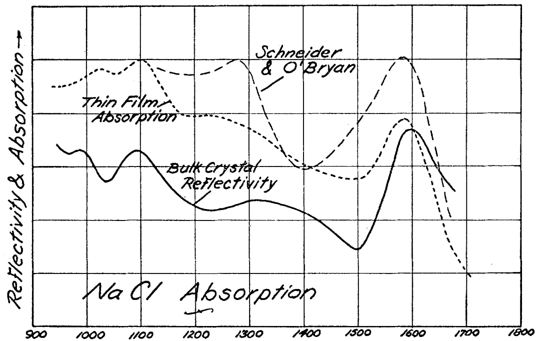

FIG. 3. Curves comparing the reflectivity and absorption measured in this work with that of Schneider and O'Bryan in NaCl. No real peak at 1280 A is observed. Later work appears to make this region even flatter.

The early measurements using this technique were made to correlate the reflectivity with the absorption. The optical arrangements used here are indicated schematically in Fig. 2. To measure the relative reflectivity, the incident light is reflected from the crystal to the phosphor as shown in Fig. 2(b), to obtain something proportional to the reflected light; for a measure of the incident light, the previous arrangement is moved out and a new one put in its place such that the beam is caught first by a phosphor and then seen by the photomultiplier by way of a front surface mirror as in Fig. 2(a). A sliding seal enables one to easily interchange the two units in front of the photomultiplier. To measure absorption (necessarily of thin films) the arrangement was changed to that of Fig. 2(c). The salt was evaporated from a clean molybdenum boat in the detector head onto a thin film of Zapon. This film could also be moved in and out of the beam from the monochromator which was incident on the end of the phosphor coated photomultiplier.

The results of these measurements on NaCl and KCl, together with a comparison of the absorption measurements of Schneider and O'Bryan, are indicated in Figs. 3 and 4. It is first of all seen that a fair agreement exists between the reflectivity and the apparent absorption, and further, that at least in KCl agreement exists between these results and those of Schneider and O'Bryan as far as the latter go. There is found here another peak in reflectivity and apparent absorption below 1000 A. The agreement with Schneider and O'Bryan in the case of NaCl is not as good, in that no pronounced maximum at 1280 A is found in either the reflectivity or absorption. In fact, with better apparatus, it will be seen that the reflectivity is even flatter than here indicated. The film laid down on a plastic substrate may behave differently than that laid down on another crystal of structure similar to its own; or the stoichiometry may be different in the two evaporated films. It should be pointed out that in neither these absorption measurements nor in those of Schneider and O'Bryan is any correction made for the reflected light, which, as will be seen, can be quite appreciable, even at normal incidence. However, the thin-film absorption measured in this work was obtained by getting not only the ratio of the transmission of the substrate alone to that of the substrate plus the evaporated layer of salt, but also by taking the ratio of the transmission of the latter film combination to that of the same combination with a further layer of salt evaporated over the first. If one

---

[11] K. Watanabe and C. Y. Inn, J. Opt. Soc. Am. 43, 32 (1953).

disregards any interference, as Schneider and O'Bryan also did, the effect of reflectivity of the front surface in the second ratio should not be present. However, the curves obtained are quite similar in both cases, showing further that the reflectivity pretty well mirrors the absorption.

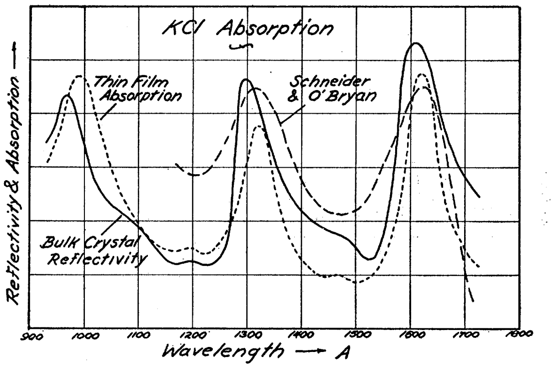

FIG. 4. Comparison of thin-film absorption and reflectivity of KCl with the absorption curve obtained by Schneider and O'Bryan.

Identification of the peaks is at this time not clear; one hopes that the proposed photoconductivity measurements will be illuminating in this regard. It is at present postulated, and experiments to be described support the notion, that the first peak is due to the exciton transition. The second peak (it can hardly be called that in the case of NaCl) is thought to be due to the valence band to conduction band transition which would presumably lead directly to photoconductivity. Seitz[12] suggests that the third peak is probably due to further ionization states of the crystals. These identifications have yet to be confirmed. It is of interest to note that the over-all absorption curves of NaCl and KCl are quite different except in the region of the first peak where they are very similar.

On the supposition that the first absorption peak is due to exciton absorption, Krumhansl suggested that it should be temperature-sensitive as in the well-known case of KI,[13] more so than the shorter wavelength absorptions. Accordingly, attempts were made to observe the reflectivity at low temperatures. Direct cooling to liquid nitrogen temperatures of the crystal in the arrangements of Fig. 2 was tried and found impractical because of the condensation of some material on the face of the crystal. In fact, interference maxima and minima could be observed in the photomultiplier output as the crystal was cooled. It was apparent that it would be necessary to surround the crystal with cold surfaces before cooling the crystal itself.

The arrangement devised is indicated in Fig. 5. A double-walled copper box-like enclosure with slits to admit light is suspended from a liquid nitrogen container. A semitransparent phosphor is used to observe the incident light and a mirror-backed phosphor for the reflected light. The visible light which these phosphors generate passes out through openings in the back of the box to the photomultiplier. The crystal (or crystals) is supported on a rotatable drum within the inner box to be moved into or out of the beam of monochromatic radiation which is reflected at about 45° on to the reflection phosphor. A position on the drum is provided for a LiF slab on which, through a slot below, it is possible to evaporate the alkali salt on the LiF for absorption measurements. With this arrangement any noticeable contamination of the surface was very slow. It was, however, possible to make measurements only to within about 50° of liquid nitrogen temperature. Nevertheless, reflectivity curves of KCl and NaCl were remade at room temperature with the box walls cold and then made at as low a temperature as could be reached with the arrangement. It was also possible to keep the crystal warm by means of a flat heater between the crystal and its copper supporting shelf in the drum to enable heating the crystal (with the box cold) to drive off any volatile films. The heater was a mica wafer coated with Aquadag and heated by a current brought in on the sides through thin sheet nickel strips crimped over opposite edges of the mica. This, however, was the reason why the minimum temperature that could be reached for the cold measurements was so high. In these measurements particular care was taken to subtract from the light readings the readings of radiation scattered from the grating. The latter were obtained by retaking each reading through a quartz filter cutting off at about 2000 A. Ideally for this, one would like a sharp variable cutoff filter to follow the monochromator wavelength setting. However, the present procedure appears to be about as satisfactory as one can hope for.

Reflectivity curves for both NaCl and KCl (crystals grown by Harshaw) at two temperatures are indicated in Figs. 6 and 7. The reflectivity is plotted in arbitrary units. To be noted are: the general rise in the reflectivity

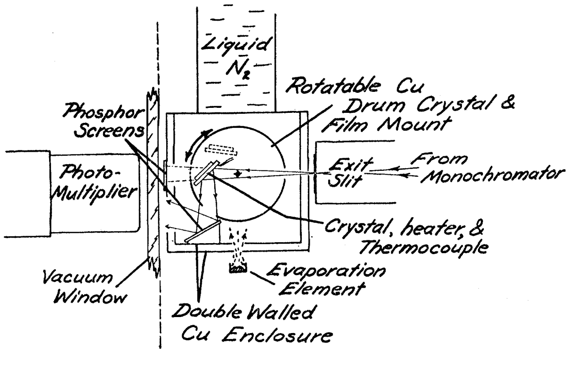

FIG. 5. Diagrammatic arrangement of apparatus used in obtaining the curves of Figs. 6, 7, and 8. Actually, several crystals could be mounted in the drum at the same time. The position of the LiF plate for carrying an evaporated film is not indicated here. Thermocouple leads and a heater lead were brought in on the axis of the drum.

---

[12] F. Seitz (private communication).

[13] H. Fesefeldt, Z. Physik 64, 623 (1930).

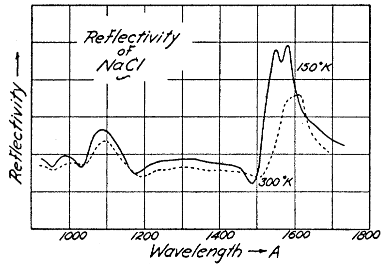

FIG. 6. Comparison of the reflectivity of NaCl at room temperature and at low temperature. The general rise in reflectivity observed in Fig. 3 below 1450 A does not appear here. Part of this may be due to the greater care in subtracting out the scattered light. However, no such behavior is seen in the KCl curves.

at low temperatures, particularly near the peaks; the absence of any real maximum between 1500 and 1200 A in NaCl at either temperature (incomplete later measurements would indicate that the high- and low-temperature curves may be closer together in this region); and the general temperature sensitivity of the first absorption in both NaCl and KCl. Besides rising to much higher values at low temperature, this peak is now double and shifted markedly to shorter wavelength, much more so than other peaks. The region below 1500 A has yet to be more carefully investigated, but extensive work has been done on the first absorption, which is the principal interest of this paper.

In order to further the evidence that reflectivity measurements can give useful information concerning the absorption positions in such crystals, an attempt was made to see the doubling of the peak in a cold film of NaCl evaporated on a LiF plate. Both the reflectivity and transmission of such a thin film were observed with the results indicated by Fig. 8. The reflectivity measurement involves three surfaces. There are the vacuum-film interface, the film-LiF interface, and finally the back surface of the LiF and its copper support (used in the reflectivity measurement). These factors are responsible for the rise in the reflectivity on the long wavelength side of the absorption peak. On the other hand, the slight suggestion of further structure on the same side of the absorption peak appearing in the curves for both NaCl and KCl in Figs. 6 and 7 cannot be so simply set aside. Its appearance, however, was never entirely consistent, in that it sometimes came up markedly and sometimes with barely a sign. It was tempting to think of it as another component in the exciton absorption, but the suspicion remained that it was due to some systematic perturbation, which has not, however, been found.

These results were encouraging enough, and the possible side structure tantalizing enough that it seemed worthwhile to pursue it further. In the meantime, Zollweg[14] was observing structure in the absorption of BaO in the exciton band and Overhauser[15] proposed a group-theoretical treatment of the expected structure of the exciton absorption. A much better and presently used arrangement was therefore designed and made, which enabled one to make reflectivity measurements at a near to normal angle of incidence to avoid possible problems with two different planes of polarization of the light at a 45° angle of incidence; measurements were also to be extended to liquid helium temperature. The new apparatus is illustrated schematically in Fig. 9. The cryostat is very small, taking only about 400 cc of liquid helium, although the liquid nitrogen reservoir around it takes considerably more. A single transfer of helium will last over two and a half hours. The crystal is clamped down to a small copper block bolted to the bottom of the helium container. The copper block support rod has an internal heater to make possible warm crystal measurements while the surrounding walls are cold. Light from the exit slit is reflected to a mirror-backed sodium salycilate phosphor seen, as in previous arrangements, by the photomultiplier. To measure the incident light another small similar phosphor, coated simultaneously and presumed identical to the first in its response, is moved in front of the crystal by a rotating system which also brings a front surface mirror up in front of the first phosphor, such that the image of the second phosphor appears at the position of the first phosphor. Thus, both phosphor positions as seen by the multiplier are the same. Were it not for the fact that the mirror is not 100% reflecting and, worse, that the reflected light phosphor is also partly seen by the photomultiplier in the retracted mirror as well as directly, absolute reflectivities would be given immediately. It is possible, however, to make a fair correction for these effects to reduce the measured reflectivity to absolute reflectivity.

The liquid nitrogen container surrounding the helium vessel is threaded at the bottom so that the small housing containing the above optical arrangement can be screwed on to it through the back opening of the detector head after one has passed the cryostat down through the detector head top extension to which it is bolted in a vacuum seal; this is indicated in the Figs. 9 and 1. Provision is made for adjustable positive stops for the mirror positions, for thermocouple leads to determine the crystal temperature, and for one heater lead, the other side of the heater being grounded internally. The shaft for rotating the mirror and phosphor is

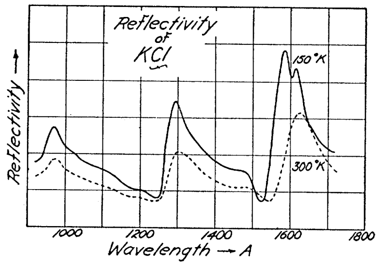

FIG. 7. Comparison of the reflectivity of KCl at room temperature and at low temperature.

---

[14] R. J. Zollweg, Phys. Rev. 97, 288 (1955).

[15] A. W. Overhauser, Phys. Rev. 101, 1702 (1956).

flexible through a bellows and is of low thermal transmission to the outside. With practice the whole apparatus can be disassembled, the crystal removed and replaced by another, the apparatus re-assembled and evacuated, all within an hour. In any such operation the crystal is kept in a desiccator after cleaving, and maintained above room temperature during the mounting process by keeping it under close incandescent lamp illumination and heating. When in the vacuum system and not in use, it was kept with the heater at about 50°C, well above the temperature of its surroundings. The back of the crystal is rough-ground flat and blackened to try to minimize back surface reflection outside the strong absorption regions; between it and its copper mounting block is an indium foil for good thermal contact. The inside of the cold enclosure is well blackened. This enclosure extends back and surrounds to keep cold most of the end-on photomultiplier which is passed into the vacuum through an O-ring seal[16] in the back plate of the detector head.

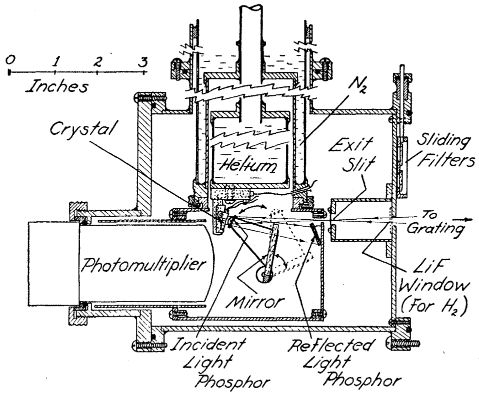

FIG. 9. Diagram of the detector head arrangement and cryostat used for determining the reflectivity at liquid helium temperature. Not labeled are the heater lead and the two thermocouple leads on the top of the crystal. They are brought out of the cold region through insulated sleeves such as is shown for the heater lead. The LiF window in front of the exit slit may or may not be waxed into position. The angle of incidence of radiation on the crystal is about 5° off the normal.

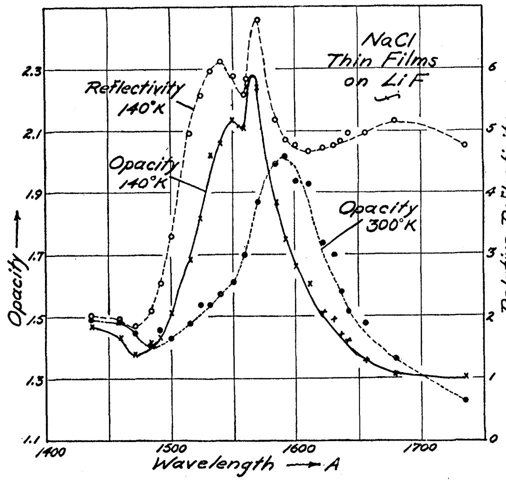

FIG. 8. Reflectivity and absorption for a thin evaporated film of NaCl. The rise at wavelengths above 1600 A is thought to be due to reflection from the surfaces back of the thin film. In this region the absorption is changing rapidly.

Extensive measurements on NaCl and KCl have now been made with this apparatus over the region of the exciton absorption. Considerable difficulty was at first met at helium temperature with unavoidable hydrogen gas getting into the detector head from the lamp, the hydrogen condensing on the helium-cooled surfaces. When the helium level would drop some, considerable condensed hydrogen would come off, decreasing the thermal insulation to the outside walls, which further lowered the helium level; and so on. The result was a sudden geyser-like eruption of the helium from the cryostat and a violent swing off-scale of the photomultiplier output current. (This last is not understood but is probably associated with a perhaps transient glow discharge initiated by the increase in pressure and the presence of high voltage below ground inside the wall of the phototube. Similar odd behavior has been observed at other times with these devices.) The difficulty has been entirely eliminated by sealing off the detector head with a thin LiF window and plugging other leaks between the detector and the monochromator; this measure has also resulted in excellent time stability of the reflectivity. An extended series of runs at 320°K, 80°K, and about 6°K made on NaCl and KCl is summarized in the curves shown in Figs. 10 and 11. The dashed curves are for polished crystals and the solid curves for cleaved crystals. As mentioned, the data taken do not give the absolute reflectivity directly. To go from the apparent reflectivity to the absolute reflectivity, two methods have been used. A reflectivity measurement is made on a warm crystal with the 2536 A line of a mercury lamp as light source. The reflectivity should be given here by $(n-1)^2/(n+1)^2$, where n is known and where one assumes that there is no contribution from the back surface, which is not quite so, even though the back surface is blackened and rough-ground. It has also been checked in the vacuum ultraviolet by measuring the incident light and apparent reflected light as usual with the lamp very well stabilized. Then, without turning off the lamp, the detector head is closed off from the monochromator, let down to air, opened, the mirror in the reflection position covered with a lamp blackened hood, the head closed, pumped down, and the reflection measurement made over again. Knowing the mirror reflectivity for visible phosphor radiation and taking lamp black to be black at 1600 A allows one to get the absolute reflectivity. The two methods are not in exact agreement, but are close enough to allow a reasonably close estimate of the absolute crystal reflectivity to be made. The reflectivity

---

[16] Johnson, Watanabe, and Tousey, J. Opt. Soc. Am. **41**, 702 (1951).

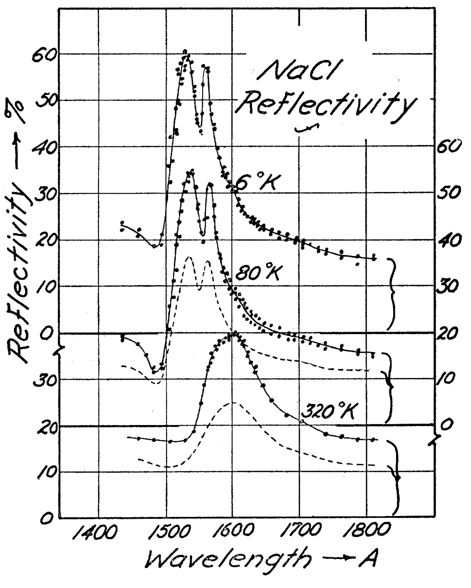

FIG. 10. Reflectivity curves over the region of the exciton absorption in NaCl at three temperatures. The dashed curves are obtained with polished crystals and the solid curves with cleaved crystals. At 6°K the points indicated were taken on the best crystal in three runs. The 80°K curve is an average of runs on two crystals, normalized to the peak reflectivity of the best crystal. The points for this are the average for one crystal and for the other, respectively, to show the spread between crystals. The room-temperature curve points are from a series of runs on the best crystal. The brackets connect the curves and their appropriate zero base ordinates.

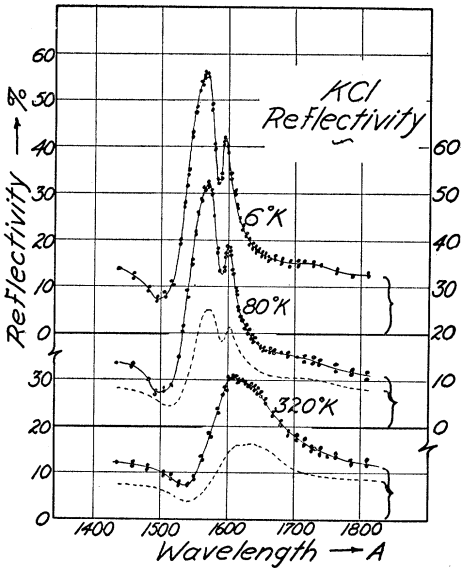

FIG. 11. Reflectivity curves over the region of the exciton absorption in KCl at three temperatures. The dashed curves are obtained with polished crystals and the solid curves with cleaved crystals. For all three curves, the points indicated were taken on the best crystal in a series of runs. Points are indicated to show something about the spread in the results. The brackets connect the curves and their appropriate zero base ordinate.

is plotted in Figs. 10 and 11. One is impressed with the magnitude of the reflectivity, which at low temperatures for NaCl approaches 60±3% and which in the case of KCl is almost as large.

The reflectivity clearly shows the absorption to have a doubled peak at low temperatures and with a suggestion still of further possible structure on the long-wavelength side of the peak. With this apparatus, the possible side structure is more consistent than previously, but it is not as striking as one would wish in order to make it positive. The small broad bump still further out from the peak on the long-wavelength side is not positive either. It occurs conceivably where any contribution from the back surface cuts out owing to the rising absorption. It is in the same region where a similar effect appears in Fig. 8. However, the crystals used here are far from being films and are of the order of 2 to 3 mm in thickness, which would seem to preclude any contribution from the back surface this close to the absorption peak. There is the pronounced shift to the shorter wavelengths at low temperatures. Assuming it to be linear, say, over the range in temperature down to 80°K, the shift amounts to about 6×10^{-4} ev per °K. The separation between the two main components in the reflectivity (taken at the peaks) is about 28 A or 0.12 ev which is in fair agreement with the 0.11-ev separation of the doublet level of the ground state of neutral chlorine.

The curves over this region have been obtained with cleaved and polished crystals grown by the Harshaw Chemical Company. The polished crystals call for comment: The cleaved crystals are almost invariably not of really high optical quality. They are, however, of definitely higher reflectivity, even visibly under ordinary illumination, than crystals which were polished to a good optical surface (though of undoubtedly poor figure). The polishing was carried out on a beeswax HCF lap using cerium oxide in a saturated solution of the salt to be polished and carried on until the lap is practically dry, followed by a light rubbing on a clean soft chamois skin. With both the KCl and the NaCl the reflectivity of the polished crystal is down about 40 to 50% from the cleaved optically imperfect crystal surface. But the structure remains much the same when normalized to the same peak reflectivity. What likely happens is that, while the polished surface is a better surface optically, the surface region is not as dense as the cleaved crystal surface region so that the intermediate and likely tapering refractive index region between the bulk material and the outside provides a better index match between the vacuum and the bulk crystal so as to effectively lower the reflectivity. There is evidence in x-ray crystal rocking curves that polished crystals are much inferior to cleaved surfaces in this respect,[17] with a broken granular surface resulting from a polish.

Work is now being carried out on mixed crystals, in

---

[17] K. V. Manning, Rev. Sci. Instr. 5, 316 (1934).

particular KCl mixed with KBr, KCl mixed with NaCl and with RbCl. The first measurements indicate that as much as 30 mole percent of KBr all but obliterates any evidence of the exciton absorption, at least as evidenced in reflectivity measurements. This will be reported on subsequently.

DISCUSSION

It is well known from optical theory that the reflectivity in an absorbing medium depends on other than the usual index of refraction.[18] Rather, in the electromagnetic equations n is replaced by the so-called complex index $\bar{n}=n(1-i\kappa)$. If one reflects light at normal incidence from a highly absorbing material, the reflecting power ρ is given by the usual Fresnel relation but with n replaced by $\bar{n}$, that is

$$\rho=\frac{\bar{n}-1}{\bar{n}+1}\frac{\bar{n}^*-1}{\bar{n}^*+1}$$

$$=\frac{(n-1)^2+n^2\kappa^2}{(n+1)^2+n^2\kappa^2}.$$

When $n\kappa$ is large this approaches unity. Presumably this is approximately the situation in the region of the strong absorption observed in NaCl and KCl. The reflectivity one observes in any spectral region is of course due to the combined effects of all the characteristic absorptions of the substance over the entire spectral domain, and involves both the resultant $n\kappa$ and n. Only in the immediate vicinity of a high absorption peak or very far from any absorption can one or the other be neglected. In the case of the absorptions in NaCl and KCl discussed above, the actual reflectivity is about 50% and not close enough to unity to assume safely that the real part of the index is negligible in comparison with the imaginary absorption part, $n\kappa$. In general one needs independent measurements on both the absorption and the reflectivity to determine the two values of the constants; or measurements of the ellipticity of reflected polarized light in the usual manner by which it is done for metals would be another.[19] Neither method appears attractive for these highly absorbing crystalline materials in the vacuum ultraviolet region. From the above work, one can really infer only the location of the absorption peaks, their widths, and their possible multiplicity.‡ It is clear from the curves obtained that the particular absorptions observed here are at least double in structure. The fact that the short-wavelength peak of the doublet is the broader of the two in both crystals, but particularly so in KCl, where it is also of greater magnitude, indicates that the short-wavelength peak may also be multiple itself.

In the bromides and iodides the long-wavelength absorption peak of the halides has from the work of Hilsch and Pohl[4] been known to be doubled, and it was supposed that only adequate resolution prevented seeing it in the chlorides. The transition involved in the exciton absorption is that of an electron going from a negative halogen to an alkali ion—the hole and the electron still being bound together. Since the ground state of the neutral halogen is a doublet, in chlorine of separation 0.11 ev, the absorption shows two peaks. On the other hand, in Hilsch and Pohl's work some of the iodides show a third peak on the short-wavelength side of the doublet, and in KI Fesefeldt[13] has shown that at low temperature a small peak comes up in between the doublet. It may well be that the counterpart in the chloride of either of these components may be responsible for the observed broadening of the short-wavelength peak. It is disappointing that better confirmation of Overhauser's prediction of a multiplicity higher than two is not obtained. On the other hand, the calculations for obtaining the relative magnitudes and positions of the five components from his theory have not yet been completed and it may well result that the others are not favorable for observation. It was also hoped that the work would tie in with some of the x-ray results in and ideas on KCl developed by Parratt and Jossem[20]; so far this has not been too promising. Their predicted absorption in KCl at about 600 A is, however, to be looked for if our present hydrogen lamp, operated instead with helium, puts out sufficient intensity to make it usable with the rather inefficient light collection and conversion system that has been used here.

The fact that the peaks do not sharpen appreciably below liquid nitrogen temperature is not too surprising in view of the high Debye temperatures of the crystals ($\theta_{\mathrm{NaCl}}=281$°K, $\theta_{\mathrm{KCl}}=230$°K). The shift to shorter wavelengths at low temperatures is presumed to be due to the lattice contraction.[21]

Finally, it may be well to point out that with reflectivities as high as measured here, occurring in any substance in a region of high absorption, one will be quite in error in quoting any quantum efficiencies or

---

[18] See, for example, the treatment in R. W. Ditchburn's *Light* (Interscience Publishers, Inc., New York, 1952), Chap. 15.

[19] R. W. Ditchburn, J. Opt. Soc. Am. **45**, 743 (1955).

‡ *Note added in proof.*—Mr. F. C. Jahoda has called our attention to the work of T. S. Robinson [Proc. Phys. Soc. (London) **B65**, 910 (1952)] in which, for polythene, he deduces curves for both n and $n\kappa$ from a reflectivity *vs* wavelength determination made at 22° from normal incidence. Use is made of concepts from network analysis where it is known that if a network is linear, the attenuation through it and the phase shift introduced by it are directly related. If one of these quantities is known over all frequencies the other can be deduced at any frequency. Robinson uses charts and techniques from Bode [*Network Analysis and Feedback Amplifier Design* (D. Van Nostrand Company, Inc., New York, 1945), Chap. 15], utilizing this property to reduce his measured reflectivity curve to curves for n and $n\kappa$. The same technique is presently being tried on our reflectivity curves over the exciton regions of NaCl and KCl.

[20] L. G. Parratt and E. L. Jossem, Phys. Rev. **97**, 916 (1955).

[21] W. Martienssen, Nachr. Akad. Wiss. Göttingen, Math.-physik. Kl. **1955**, 257.

absorption constants in an absorption process where allowance has not been made for the reflection loss.

SUMMARY

The exciton absorption of KCl and NaCl observed in reflected light would seem to make useful this method of investigating the absorptions of single crystals as opposed to transmission techniques through uncertain thin evaporated films of the crystal salt.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the help of various people in the work, including particularly helpful discussions with A. W. Overhauser, J. A. Krumshansl, L. G. Parratt, and E. L. Jossem. Mr. J. W. Taylor has aided in some of the measurements. Thanks are also due to Mr. J. P. Gilvey for help in supplying and handling liquid helium.

PHYSICAL REVIEW VOLUME 105, NUMBER 1 JANUARY 1, 1957

Magnetic Structures in Copper-Manganese Alloys*

David Meneghetti† and S. S. Sidhu
Argonne National Laboratory, Lemont, Illinois

(Received September 24, 1956)

A neutron diffraction study of a series of substitutional solid solutions up to 85 atomic percent manganese in copper has shown that at about 13 atomic percent manganese, a broad intensity maximum appears in the region of (100) reflection of the face-centered cubic pattern of copper. A correlation of this maximum with the magnetic attraction of the specimens indicates that it is at least in part due to short-range magnetic order. Its intensity decreases at compositions greater than 50 atomic percent manganese. Above 69 atomic percent manganese an antiferromagnetic structure is observed and is interpreted as due to an antiferromagnetic coupling between manganese atoms as the manganese concentration becomes predominant.

I. INTRODUCTION

THE copper-manganese alloy system is particularly suited for study by neutron diffraction. In the continuous substitutional solid solutions[1–3] from copper-rich to manganese-rich phases, manganese atoms have a predominance of unlike and like atoms, respectively, as neighbors. Copper being diamagnetic and manganese paramagnetic it is of interest to determine if the magnetic moments of the manganese atoms and their alignments are affected by such spatial arrangements of the two kinds of atoms. The presence or absence of magnetic or antiferromagnetic structures and the dependence of paramagnetic scattering upon composition may be observed. In addition, as the coherent neutron scattering amplitudes of copper and manganese nuclei are opposite in sign,[4] superstructure lines due to atomic ordering in the alloys, if present, should be observed much more readily[5] than with x-rays[6] for which the atomic scattering factors are of nearly the same magnitude.

The magnetic susceptibility of the copper-manganese system has been reported[7] as having a maximum in the region of 22 atomic percent manganese. At liquid nitrogen temperature this maximum increased by a factor of about seven; whereas, only a small increase occurred in the remainder of the curve. Since neutrons can be coherently scattered by magnetic structures,[8] the neutron diffraction patterns may enable the reported magnetic susceptibility characteristics to be interpreted in terms of orderings of atomic magnetic moments.

II. EXPERIMENTAL PROCEDURE

The chemical and x-ray analyses of the samples used in this investigation are given in Table I.

Table I. Chemical and x-ray analyses of the alloys.

Sample	Atomic percent Mn	Cu	Phase	Lattice parameters a_0	c_0
Cu		100	f.c.c.[c]	3.61 A	
11 Mn−89 Cu	10.5	89.4		3.64 A	
13 Mn−87 Cu[a]	12.7	87.2		3.65 A	
18 Mn−82 Cu	17.5	82.5		3.66 A	
33 Mn−67 Cu[a]	33.2	66.9		3.72 A	
48 Mn−52 Cu	47.7	52.3		3.75 A	
48 Mn−52 Cu[b]	48.4	51.7		3.75 A	
69 Mn−31 Cu	69.0	31.0		3.75 A	
75 Mn−25 Cu	74.6	25.4	f.c.t.		
85 Mn−15 Cu	85.1	14.9	f.c.t.	3.76 A	3.64 A

[a] Commercial samples.
[b] Quenched sample.
[c] f.c.c.: face-centered cubic; f.c.t.: face-centered tetragonal.

---

* Work performed under the auspices of the U. S. Atomic Energy Commission.

† Part of a thesis presented by D. Meneghetti in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Illinois Institute of Technology, 1954.

[1] E. Persson, Z. physik. Chem. **B9**, 25 (1930).

[2] Dean, Long, Graham, Potter, and Hayes, Trans. Am. Soc. Metals **34**, 443 (1945).

[3] Dean, Potter, Long, and Huber, Trans. Am. Soc. Metals **34**, 465 (1945).

[4] E. O. Wollan and C. G. Shull, Phys. Rev. **73**, 830 (1948).

[5] C. G. Shull and E. O. Wollan, Phys. Rev. **81**, 527 (1951).

[6] L. D. Ellsworth and F. C. Blake, J. Appl. Phys. **15**, 507 (1944).

[7] S. Valentiner and G. Becker, Z. Physik **80**, 735 (1933).

[8] Shull, Strauser, and Wollan, Phys. Rev. **83**, 333 (1951).