The origin of the infrared activity of rock salt is discussed in terms of the free vibrations of the crystal. Experimental data on the Reststrahlen frequencies and on the frequency displacements of scattered radiation are used to explain the spectroscopic behavior of rock salt in the near infrared.

Rock salt was one of the first minerals of which the crystal structure was established by x-ray analysis. Its structure may be described in simple terms as made up of two interpenetrating lattices, each composed of atoms of one kind. The sodium atoms in one lattice are surrounded by six chlorine atoms in the other lattice and vice versa, in such manner that the grouping exhibits cubic symmetry. The sodium and chlorine atoms appear interspersed with each other in the cubic planes of the structure, while in the octahedral planes they appear separately in alternate layers.

The transparency of rock salt over a wide spectral range extending from 0.2 to 10 $\mu$m makes it a material of first-rate importance in applied optics and especially for use as dispersing prisms in the infrared. The dispersive power of rock salt is very low, between 1 $\mu$m and 5 $\mu$m, but improves at greater wavelengths. On the other hand, the absorption which is negligible at 10 $\mu$m becomes sensible at 13 $\mu$m and increases rapidly beyond 15 $\mu$m. Hence, rock salt may best be used as a prism material for infrared spectroscopy between 7 $\mu$m and 14 $\mu$m. It ceases to be useful beyond 15 $\mu$m.

It is well known that rock salt exhibits, in the region of long wavelengths, a high reflecting power which reaches its maximum value of about 90% at 54 $\mu$m. The strength of this reflection falls off rapidly at shorter wavelengths and is negligibly small for all wavelengths less than 33 $\mu$m. The fall is less rapid for wavelengths greater than 54 $\mu$m and the reflecting power reaches a limiting value of about 20% at 100 $\mu$m. These facts call for explanation; in particular, it may be asked why, at 15 $\mu$m which is outside the spectral region of strong reflections, the absorbing power is nevertheless large enough to impair the usefulness of the material for infrared spectroscopy.

It is proposed in this paper to review briefly the contents of a memoir by the author which has been recently published and in which the spectroscopic behavior of rock salt has been discussed in detail.1

The Free Vibrations of the Structure

The dispersion, absorption, and reflection of infrared radiation by a crystal are effects arising from the interaction of the electromagnetic field in the radiation with the structural units composing the crystal. As a first step toward an understanding of these effects, it is necessary to consider the nature of the spectrum of the free or spontaneous vibrations of these structural units. We may deduce their modes and frequencies by the methods of classical mechanics. For this purpose, the atomic nuclei may be regarded as simple mass particles and the electronic clouds surrounding them as massless springs which hold the structure together. The relevant theory is fully set out in the memoir cited above and it is sufficient here to state the results to which it leads.

It emerges that the vibrational mode of highest frequency of the rock salt structure is one in which the atoms of sodium and chlorine oscillate against each other in opposite phases. Eight other modes of free vibration are also possible. They may be described simply in terms of the crystal structure: four of the modes are oscillations of the cubic layers, while the other four modes are oscillations of the octahedral layers, the movement alternating in phase from layer to layer, and being either normal or tangential to those layers. Since the oscillations of the sodium and

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chlorine atoms may be either in the same phase or in opposite phases, we have four modes for the cubic layers and four modes for the octahedral layers, and hence eight in all. The oscillations of the sodium and chlorine atoms located in the same cubic layers would be coupled with each other. But the oscillations of the sodium and chlorine atoms, appearing as distinct layers in the octahedral planes, would be independent.

**The Origin of Infrared Activity**

We next proceed to consider the relation between the free vibrations of the structure of the crystal and the effects arising from the passage of infrared radiation through it. The electric field in the incident radiation acts both on the positively charged nuclei and on the negatively charged electrons. But in all the modes of vibration with which we are concerned, there are as many positively charged nuclei moving in one phase as there are others moving in the opposite phase. It can be shown that, as a consequence, the displacements of positive charge when totaled up cancel out in all the modes under consideration. Hence, the free vibrations of the structure cannot be excited by the forces exerted by the field on the atomic nuclei. Necessarily, therefore, the movements of the atomic nuclei can have no effect on the radiation passing through the crystal. We conclude that the infrared activity of the crystal arises solely by reason of the forces exerted by the field on the negatively charged electrons and of the resulting movements; such activity is only possible when the displacements of negative charge produced do not cancel out when summed up over each structural unit.

Since the electrons are held in position by their interactions with each other and with the positively-charged nuclei, the displacements of negative charge induced by the field would necessarily disturb the nuclei from their positions of equilibrium. But the nuclear movements thus arising would not contribute to the infrared activity. Thus, while in the free vibrations of the structure, the massive, positively charged nuclei play the leading role and the electrons a subsidiary one, the situation is reversed in respect of the infrared activity, the electrons here playing the leading role and the nuclei a subsidiary one. In other words, the spectrum of free vibrations and the spectrum of infrared absorption are essentially different in their nature and origin. Both being properties of the same structure, we may expect to find some resemblances, but nothing in the nature of an identity or complete correspondence is to be expected.

**The Reststrahlen Reflections**

The considerations set forth above indicate that the mode of vibration in which the sodium and the chlorine atoms oscillate in opposite phases would be that exhibiting by far the strongest infrared activity. Their approach and recession would be accompanied by a periodic movement of the electronic cloud located between each pair of nuclei. The effects due to the displacements of electric charge in the successive cells of the structure would be additive and would thereby attain a large magnitude. Indeed, the activity may be expected to be so great that secondary radiations would emerge from the units of the structure along the external boundary of the crystal and conspire to give a powerful surface reflection. There would also be a strong absorption and extinction of the radiation actually penetrating into the crystal.

As a matter of actual observation, the surface reflection appears with great strength between 50 μ and 60 μ, its maximum of intensity being at 54 μ. On the other hand, the minimum of transmission by very thin films of rock salt appears at about 60 μ, being thus displaced a little further into the infrared. In what follows, we shall take 56 μ to be the wavelength corresponding to the frequency of the strongly active mode of free vibration of the rock salt structure.

**Infrared Activity of Higher Orders**

The absorption of infrared radiation arises when the electromagnetic energy of the field is taken up and transformed into vibrational energy in the crystal. When the frequencies of the field and the mechanical vibration are identical, a quantum of radiational energy changes over to a quantum of vibrational energy. There are also other possibilities: the energy of the radiation taken up by the crystal may appear as two, three, or a larger number of quanta of vibrational energy. Thus, we are led to expect, besides the intense absorption around 50 μ, a series of other absorptions around 28 μ, 19 μ, and 14 μ, respectively. They may be referred to as the absorptions of the second, third, and fourth orders, respectively. The possibility of observing the higher orders of absorption arises by reason of the first-order absorption being itself of great strength. The absorptions of higher order would necessarily be weaker and of progressively diminishing strength with increasing order. Nevertheless, when the absorption path is sufficiently increased, their effect on the transmission should be observable.

That the lack of transparency of rock salt at wavelengths greater than 15 μ, which renders it unusable as material for dispersing prisms, is due to these absorptions of higher order may be inferred from the observed facts of the case. The absorption at 14 μ is noticeable when the thickness of the plate is 5 cm or more, but it ceases to be significant when the absorption path is reduced to 3 cm or less. Yet in this range of thickness, there is a complete cutoff of the incident
radiation commencing at 19 µ and extending to greater wavelengths. Reducing the thickness to 15 mm produces but little observable change in this behavior, the wavelength of cutoff drifting slightly to 20 µ. Not until the thickness is reduced to 1 mm or so does the transmission at 19 µ become at all comparable with that observed at 14 µ with far larger thicknesses. To obtain such a free transmission at 28 µ, the path has to be further reduced to about 50 µ, while only films which are a few microns thick would give an observable transmission at 56 µ. It is evident from such facts that we are dealing with absorptions of altogether different orders of magnitude in these four cases.

The Infrared Activity of the Other Modes

We have now to consider the eight other modes of free vibration mentioned earlier. By reason of the vibrations being in opposite phases in the alternate layers, the displacements of electric charge in all the eight modes cancel out in the first approximation. But in the case of the four coupled oscillations of the sodium and chlorine atoms appearing in the cubic layers, the displacements of electric charge do not cancel out in the second approximation; there is a surviving component having twice the frequency of the mode under consideration. Hence these coupled vibrations would be strongly infrared active, but with doubled frequency in each case.

Taking 56 µ as the wavelength of maximum infrared activity, the wavelengths corresponding to the four modes referred to may be theoretically estimated to be 66 µ, 78 µ, 90 µ, and 108 µ, respectively. The halved wavelengths at which their second-order activity would manifest itself would therefore be 33 µ, 39 µ, 45 µ, and 54 µ, respectively.

The foregoing figures enable us to understand why the spectral region in which the strong surface reflections appear extends toward shorter wavelengths and that of the most highly active mode. It would, therefore, fall off steadily as we recede from the mode having the highest activity towards lower frequencies and longer wavelengths.

The Spectrum of Light Scattering

The picture of the dynamical behavior of the rock salt structure and its relation to the infrared behavior of the crystal briefly summarized above finds a striking confirmation in the results of two other entirely independent lines of research. The first is the evaluation of the thermal energy of rock salt over the whole range of temperatures extending from absolute zero upwards, the theoretically determined and spectroscopically confirmed frequencies of vibration of the structure and their respective degeneracies being the basis of the calculation. To enter into this subject would take us beyond the field of applied optics; we shall therefore here only deal with the other line of investigation. This is a spectroscopic method closely related to the field of infrared studies, viz., the study of the spectral shifts observed in the scattering of monochromatic light in its passage through rock salt.

The frequency shifts observed in the scattering of light arise from the periodic changes in the optical scattering power of the structural units in the crystal. These changes are produced by their internal vibrations and hence the observed shifts may usually be identified with the frequencies of the vibrations. But in a particular class of cases, frequency shifts are recorded with notable intensity in the spectrum of the scattered light, which are double the frequency of the vibrations of the structure. The frequency shifts observed with rock salt are all of this kind, and the reason for this is not far to seek: In each of the nine modes of free vibration, we find a sodium atom approaching a chlorine atom on one side and simultaneously receding from a chlorine atom on the other side, and vice versa. The increased scattering power due to the approach is set off by the decrease due to the recession and cancels out in the first approximation. But in the second approximation, there is a residue left over, and this
would evidently be periodic but with a doubled frequency.

The spectrum of the scattering of light in rock salt was successfully recorded several years ago by Rasetti in a noteworthy investigation. The microphotometer record of the spectrum obtained by him is reproduced from his paper as Fig. 1. The frequency shifts in wavenumbers have been marked in the figure. The record shows the position of the exciting radiation (2536.5 Å) from a water-cooled mercury are enclosed in quartz which was placed between the poles of an electromagnet in order to eliminate the self-reversal of the emitted radiation. The frequency shifts were both negative and positive, and they appeared respectively to the left and to the right of the position of the exciting radiation in the microphotometer trace.

The negative shifts are recorded with great intensity and, being overexposed in the original spectrogram, are not so clearly resolved from each other in its microphotometer trace as the positive shifts. These latter appear as successive steps in the record, and the respective frequency shifts are easily read off from their displacements with respect to the λ 2536.5 line. It will be seen that all the nine different frequency shifts may be clearly recognized. Their values as read off from the record on the right-hand side are in excellent agreement with the doubled frequencies of the respective modes, as theoretically estimated.

The relative intensities of the nine negative-frequency shifts as indicated by Rasetti's microphotometer record are also in satisfactory accord with the estimates based on the nature of the individual modes and their respective degeneracies. It should be mentioned the frequency shifts of ±235 cm⁻¹ stand out in Rasetti's original spectrogram as sharply defined lines. They represent the doubled frequency of vibration of the chlorine atoms located in the octahedral layers in which the movements are parallel to these layers. The notable intensity of the 235 cm⁻¹ line is a consequence of the eightfold degeneracy of the mode.

Reference
31-6 June 7
International Television Conference, London
Institution of Electrical Engineers, Savoy Place,
London, W.C.2, England
late
Interphoto Congress, Copenhagen International
Photography and Cinematography Dealers
Association, Steienvorslet 63, Basel 10, Switzerland
late
Washington Symposium on Use of Artificial Satellites
for Geodetic Purposes International Association
of Geodesy, 18 rue Auber, Paris 15, France
late
Journées de la Lumière, Grenoble W. Bing, Assoc.
Française de la Lumière, 4 rue Ed.-Roussie, Paris
14e, France
June
4-8 French Soc. of Physical Chemistry, Paris Secrétaire
Général, Société de Chimie Physique, 10 rue Vau-
guinet, Paris 6e, France
5-8 24ème Congrès Annual du AMS Sécrétariat, 1 rue J.
Boissier, Paris XV, France
7-10 Canadian Association of Physicists 17th Annual
Congress, Hamilton, Ontario,
11-14 Instrument Society of America, Seattle, Wash.,
Instrument-Automation Conference and Exhibit
11-15 Columbus Symposium on Molecular Structure and
Spectroscopy K. A. Oeljen, Dept. Physics, Ohio
State University, Columbus 10, Ohio
18-22 Eindhoven Congress on Magnetic and Electric
Resonance and Relaxation J. J. Kroon, Natur-
undbrugk Laboratorium, N.V. Philips' Gloe-
lampenfabriek, Eindhoven, Netherlands
18-22 International Conference on Spectroscopy, Univ.
of Maryland B. F. Smerben, National Bureau of
Standards, Washington 25, D.C.
19-21 APS Summer Mtg., Evanston, Ill. K. K.
Darrow, Columbia Univ., New York
19-29 ASTM National Meeting and Apparatus Exhibit,
Statler Hotel, New York ASTM, 1916 Race
St., Philadelphia 3, Pa.
24-29 Institute of Nuclear Magnetic Resonance, Buffalo
H. A. Symons, Chemistry, Canisius College,
Buffalo 8, N.Y.
25-30 Copenhagen Symposium on Electromagnetic Theory
and Antennas H. Lottup Knudsen, Oster Vold-
gade 10 G, Copenhagen K, Denmark
July
—
Munich Symposium on Crystallographic Computing
D. W. Smith, International Union of Crystal-
lography, c/o Mathematisches Institut., Univ. of
Groningen, Gelid kondakple 4, Groningen, Nether-
lands
8-14 6th International Conference on Glass, Washington,
D.C. C. H. Hahn, General National Committees,
c/o Glass Section, National Bureau of Standards,
Washington D.C.
9-11 11th International Astrophysics Symposium, Liège
P. Swings, Inst. of Astrophysics, Sciensia, Belgium
9-20 Summer Course in Optics Inst. of Optics, River Campus
Station, Rochester 30, N.Y.
10-20 Summer Course on Techniques of Infrared Spectro-
scopy Director, Center for Continuation Study,
Univ. of Minn., Minneapolis 14, Minn.
16-19 International Colloquium on Novov, Novoids and
Supernovv, Lyons J. Dufay, U. de Lyons, rue de
Cavenne, Lyons, France
16-20 IUPAC Conference on Paramagnetic Resonance,
Jerusalem W. Low, Hebrew Univ., Jerusalem,
Israel
16-20 International Conference on the Physics of Semi-
conductors, Exeter. IPPS, 47 Belgrave Square,
London, S.W.1, England
25-31 Symposium in Commemoration of Fiftieth An-
iversary of the Discovery of X-Ray Diffraction
and of Crystal-structure Analysis, Munich F.
Bopp, Inst. für Theoretische Physik, Sch-ilingsstr.
4-8, Munich, Germany
August
—
3rd International IUPAC Symposium on X-ray,
Microscopy and X-ray Microanalysis, Stanford
H. M. Pattee, Dept. Physics, Stanford Univ.,
Stanford, Calif.
5-11 2nd International Congress on Radiation Research,
Harrogate A. Howard, Mount Vernon Hospital,
Northwood, Middlesex, England
0-10 Society of Photographic and Instrumentation
Engineers Meeting, Biltmore Hotel, New York.
0-17 MIT Summer School Course J. M. Austin 7-103,
13-15 Interdisciplinary Conference on Electromagnetic
Seatingter, Potsdam, N.Y. M. Kerker, Clarkson
College, Potsdam, N.Y. 3 Medizinische Optik,
Arnulfstr. 205, Munich, Germany
14-16 Boulder International Conference on Precision
Electromagnetic Measurements G. Birnbaum,
Higher Research Lab., Malibu, Calif.
14-18 Fisk Infrared Summer Course Director, Fisk In-
frared Institute, Fisk Univ., Nashville, Tenn.
19-26 Sixth General Assembly of International Commissiol
For Optics and Congress on Image Formation,
Munich H. Scholcher, Institut für Medizinische
Optik, Arnulfstr. 205, Munich, Germany
21-24 International Symposium of Far Infrared Spectros-
copy, Sheraton-Gibson Hotel, Cincinnati F. F.
Bendley, ASD, Wright Patterson AFB, Ohio
21-28 Copenhagen International Congress on Acoustics
P. H. linters. Tekniko Højskole, Oestervolgade
10, Copenhagen, Denmark
27-29 7th Symp. Ballistic Missile and Space Technology Aerospace Corp., P.O. Box 95085, Los Angeles 45,
Calif.
27-29 APS Summer West Mtg., Seattle, Wash. H. A.
Shuuk, Physics, Univ. of Calif., Berkeley 4,
Calif.
27-30 American Astronomical Society Meeting, Yale
Univ. H. Smith, Yale U. Observatory, New Haven,
Conn.
27-31 Infrared Gordon Conference, Meriden, N.H.
27- Sept. 1 2nd International Conference on Information
Processing, Munich IFIPS, 1634 Arch St.,
Philadelphia 3, Pa.
30-Sept. 5 Symposium on Photo Interpretation, Deflt
Commission VII Intl. Training Centre for Aerial Survey,
Kanaaaweg 3, Deflt, Netherlands
September
—
British Assoc. Advancement Science Intl’l Meeting,
J. Manchester G. Allen, Burlington House, London,
W. 1, England
3-7 Brussels International Symposium on Information
Theory F. L. Stumpers, Philips Research Labs,
Eindhoven, Netherlands
5-7 Emittance and Reflection of Radiation from Various
Materials and Space Applications Univ. of
Dayton
7-12 Kyoto International Conference on Crystal Lattice
Defects R. R. Hasiguti, Univ. Tokyo, Bunkyo-
ku, Tokyo, Japan
9-14 Dallas Technical Conference of the Illuminating
Engineering Society
10-15 IUPAC Tokyo International Symposium on Molecu-
lar Structure and Spectroscopy Science Council
of Japan, Ueno Park, Tokyo, Japan
16-20 Electromechanical Society Meeting, Statler Hilton
Hotel, Boston, Mass.
17-19 9th Ottawa Symposium on Applied Spectroscopy
B. Farrar, J. T. Donald & Co. Ltd., 1181 Guy St.,
Montreal 26, Que., Canada.
17-22 6th Intl. Congress on High Speed Photography,
Scheveningen J. G. A. de Graaf, 14, Burgemeester
de Monchyplein, The Hague, Netherlands
24-28 Union of German Physical Societies, Stuttgart
H. Franke, Verband Deutscher Physik. Gesell.,
Gänseheide 15A, Stuttgart, Germany
October
—
Infrared Information Symposium Fall Meeting
Eastern States
—
URSI Montreal Meeting M. G. George, Thayer
School of Engineering, Dartmouth College, Hanover,
N.H.
—
Varian Annual NMR-EPR Workshop Varian
Assoc., Hansen Way, Palo Alto, Calif.
4-6 Optical Society of America 47th Annual Meeting,
Manger Hotel, Rochester Hilda Kinglake, 50
Westland Ave., Rochester, N.Y.
5 OSA Annual Business Meeting, Manger Hotel,
Rochester, N.Y.
15-19 Instrument Society of America 17th Annual Instrument-
Automation Conference and Exhibit W. H.
Kuchnich, 3156th Ave., Pittsburgh 22, Pa.
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