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The Development and Exploitation of the Very-far Infra-red Region of the Spectrum

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Abstract. The development of techniques for the very-far infra-red during the past decade is reviewed including sources, both conventional and laser, filters, spectrometers and detectors. A new design of fast single-crystal Ge bolometer is described.

Various recent applications of very-far infra-red techniques in physics research are discussed including molecular and solid-state spectroscopy, superconductivity, and some new work on absorption of compensated semiconductors and its relationship with impurity-band conduction.

1. The Spectral Gap

It is a long time since there was serious doubt that there is any essential difference between infra-red radiation and very short radio waves or that the one would merge continuously into the other. Until fairly recently, however, there has remained a largely unexplored region of the spectrum extending for over a decade of wavelengths from about 200 μm to 2000 μm. With the discovery of the residual rays or *reststrahlen*, and in particular through the work of RUBENS and NICHOLS [1], the infra-red spectrum was extended to about 300 μ though few measurements of the physical properties of matter at these wavelengths were made. In the meantime, following the work of Hertz, various attempts were made towards the end of the 19th century to generate radiation having wavelengths in the infra-red by radio techniques. It was not, however, until 1923 that the first convincing demonstration was given by Nichols and Tear [2], who produced Hertzian waves with a wavelength of the order of 220 μm which they measured by means of a diffraction grating. A year later Glagolewa Arkadiewa [3] produced radiation of about 90 μm wavelength by using small Hertzian oscillators in the form of brass filings. This radiation is very similar to the infra-red radiation emitted from a hot body, being incoherent and, in electrical terminology, rather like wide-band noise. It is not until quite recently that *coherent* radiation in the far infra-red has been generated.

The essential difference between normal infra-red radiation and the radio waves and microwaves with which we are familiar turns on just this question of coherence – that is, the ability to specify a phase in a wave-train. Wavelengths of the order of 300 μm can now be generated as harmonics of coherent oscillators such as the klystron, and with the advent of the laser coherent wave trains can be generated even in the visible region of the spectrum. At only a few specific frequencies have lasers operated in the far infra-red. These we shall discuss later.

A great step forward was taken in 1934 when CLEETON and WILLIAMS [4] demonstrated the interaction of radio waves, in the range of wavelengths 1–4 cm, with molecules, finding characteristic absorption lines as for radiation in the visible and near infra-red regions of the spectrum. This led to the field of research known as microwave spectroscopy which has done so much to refine our knowledge of molecular structure. It is not with this field that we shall be concerned but with the range of wavelengths lying between the short microwaves (1–3 cm) and the far infra-red (15–100 μm), namely the wavelength range 100–1000 μm now generally called the very-far infra-red.

There have been two approaches to this spectral region, as might be expected, one from above and one from below on the wavelength scale. The approach from the microwaves has been to develop better methods of harmonic generation and primary sources giving greater power at shorter wavelengths. By these techniques, tunable narrow-band sources have been available to wavelengths of the order of 300 μm, though it must be admitted that the power available at wavelengths shorter than 800 μm is very small. To consider the development of these techniques in detail would take us too far afield and we shall concentrate on the second approach, that of extending optical techniques to longer wavelengths. The most interesting developments at the moment consist of a marriage of these two approaches and we shall later discuss some novel methods of detection which involve both.

2. The Very-far Infra-red

There is now, as we have seen, no mystery about this region of the spectrum. There are, however, very great difficulties in making physical observations in it. It is with these and with developments that have enabled many of them to be overcome, so as to yield new information on the physics of materials, that we shall be concerned. We may state at once that the main difficulty arises from the small amount of energy available from conventional sources compared with the vastly greater amounts emitted at shorter wavelengths. Not only are we short of energy but we have great difficulty in getting rid of the unwanted radiation at shorter wavelengths. This is particularly troublesome when we have overlapping orders as in a grating spectrometer.

Advances both in conventional source design and in filtering techniques have been of great assistance but more spectacular is the development of 'line' sources in the form of lasers [5]. There have also been remarkable advances in detection techniques and consequently in the layout of spectrometers. As a result, the subject has advanced from the stage of being concerned mainly with the properties of the radiation itself to its use in spectroscopy and other applications. We shall first of all describe some of these advances in technique and then discuss some of the recent physics research carried out by their means.

3. Sources of Radiation

Although a hot silicon carbide rod (known as a 'globar') is still used as a source in the very-far infra-red it has been largely replaced by the high-pressure mercury-vapour lamp for wavelengths greater than 100 μm. One of the unsatisfactory and troublesome features of this source is the so-called 'channel spectrum'. This is due to periodic variations in intensity as a function of wavelength due to interference between radiation from front and back surfaces of the quartz envelope. 'Dimpling' the envelope helps, but by no means eliminates this trouble.

Lasers [5] as sources are just beginning to be used in the very-far infra-red. The available radiation is unfortunately confined to a small number of lines. At present, these sources are untunable except over a very narrow range. The only type in common use is the HCN laser [6] first introduced by H. A. Gebbie and his colleagues, giving a strong line at 337 μm [6]. (This line was formerly thought to be due to the CN radical and so this laser is sometimes referred to as the CN laser.) A number of other spectral lines have now been found to give laser action in the very-far infra-red, mainly due to work of A. Javan and his colleagues [6]. A list of currently available lines is given in Table 1, derived from the papers listed under Ref. (6) where the wavelengths are given much more accurately, sometimes to seven significant digits.

Table 1

Laser lines in the very-far infra-red

Approximate wavelength (μm)	Source
118	H_2O laser
190 195 204	DCN in $C_2N_2 + D_2O$ laser
284 311 337	HCN in $C_2N_2 + H_2O$ laser
375 373	$CH_3CN + H_2O + He$ laser

A line source has naturally great advantages over wide-band sources, not the least being absence of unwanted radiation in higher orders. Indeed, as found in microwave spectroscopy, if the line is narrow, greater resolution can be obtained by scanning the line if its frequency is variable, than with dispersing instruments like grating spectrometers. The rewards to be obtained from the use of tunable line sources is so great as to justify a great deal of effort in their development.

The number of lines available, although increasing rapidly, is still too small to give adequate coverage of the spectrum and some way must be found of interpolating between them, i.e. of scanning them over an appreciable frequency range. At present, the lines give c. w. powers of the order of a few mW and considerably greater pulsed powers. By mixing with microwave power derived from a klystron or other source, sum and difference frequencies may be generated as we shall see in Section 10. This gives, in principle, a tunable source, since the microwave frequency can readily be changed. The trouble at the moment is that mixers for this frequency range are rather inefficient so that only very small powers at the sum and difference frequency are generated. As better mixers become available this technique should provide usable sources. Even though the power is small the fact that it is concentrated in a narrow line can give a high power per unit wavelength interval, and sources of this type are likely to play a large part in the spectroscopy of this region in the future.

4. Filters

A number of advances have been made in the past few years in the design of filters to cut off the strong unwanted short-wave radiation. Nearly always one uses crystal quartz in the form of a sheet or lens to absorb wavelengths between 4.5 μm and 40 μm. Along with this, a sheet of black polyethylene about 0.1 mm thick is used to cut off all wavelengths less than about 7 μm.

For the elimination of longer wavelengths one or more of several different kinds of filter are used. The familiar *reststrahlen* reflection filters are still commonly used but there is now an increasing use of longwave pass transmission filters. These depend on the strong absorption by optical lattice vibrations – the so-called *reststrahlen* absorption, and have been highly developed by YAMADA, MITSUISHI and YOSHINAGA [7].

It is frequently necessary to cool these filters, even to liquid helium temperatures, especially when cooled detectors are used, and this has the advantage of sharpening up their long-wave pass characteristics as shown by ZWERDLING and THERIAULT [8]. Typical transmission curves for two such filters are shown in Figure 1. These filters, used with crystal quartz and black polyethylene, provide complete cut-off for radiation of wavelength less than the 'cut-on' wavelength of the filter.

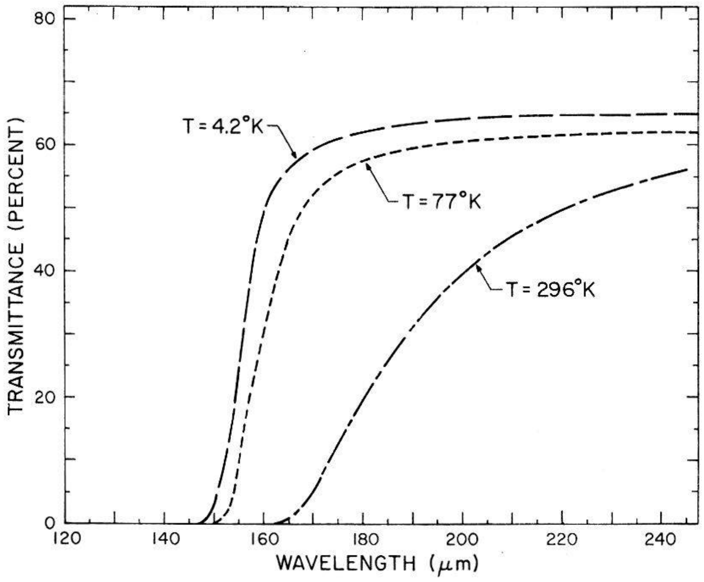

Figure 1

Transmittance of long-wave pass filters containing alkali halide powders in polyethylene at various temperatures (after ZWERDLING and THERIAULT [8]).

The use of diffraction gratings as filters depends on their property of reflecting specularly wavelengths considerably longer than the ruling spacing into the undiffracted zero-order spectrum, whereas the radiation of shorter wavelength is dispersed. Filters of this kind and various other types depending on interference, selective refraction and scattering have been described by SMITH, JONES and CHASMAR [9].

Reflection filters consisting of two sets of parallel wires at right angles, forming a mesh, are now also coming into use in the very-far infra-red. These filters have been described by Mitsuishi *et al.* [10] and by Vogel and Genzel [11]. The latter used electroformed meshes which appear to give a slightly steeper cut-on characteristic. A number of these are generally used in series and, when this is done, they provide a very satisfactory long-wave pass filter.

We should emphasise that filtering in this region of the spectrum is not easy and various combinations of filters are normally required to obtain satisfactory elimination of undesired radiation. This is of vital importance since if even a small amount is left it can give quite misleading results.

5. Spectrometers for the Very-far Infra-red

It must be admitted that some of the delay in opening up this region of the spectrum has been due to the lack of suitable spectrometers. Even now there is a distinct lack of really suitable commercial spectrometers for the very-far infra-red, and most workers in the field have designed and constructed their own instruments. There are indeed spectrometers such as the Beckman Instruments IR 11 and Perkin Elmer 301 which are fairly conventional apart from the special arrangements for filtering. They can be operated either as single-beam or double-beam instruments but are not mounted in a vacuum enclosure, depending on flushing with dry nitrogen to get rid of the very troublesome water-vapour absorption. While this is fairly effective when double-beam working is possible, it is somewhat unsatisfactory for single-beam operation. Unfortunately, for the long-wave end of the spectrum only single-beam operation is possible, due to lack of energy. Some Japanese vacuum instruments are, however, becoming available commercially, based on designs of Yoshinaga [12] and his colleagues.

Space does not permit us to describe the many interesting and novel arrangements that have been used by individual workers. Some of these have been discussed by Smith, Jones and Chasmar (Ref. [9], Ch. 11). Two spectrometers are, however, worthy of special mention, both being vacuum instruments. The first uses the Czerny-Turner optical system (see Ref. [9]) with two spherical mirrors and has been designed and used by Kneubühl, Moser and Steffen [13]. The second uses a single large mirror and an optical arrangement similar to that of the Ebert system (see Ref. [9]). It has been designed and used by Richards [14]. Both instruments use metal light pipes to conduct the radiation from the foci of the mirrors to the detector. This is a novel feature which has come into common use in the very-far infra-red.

The most striking development in spectrometers in recent years is undoubtedly the introduction of the Fourier-transform spectrometer. This has proved particularly useful in the very-far infra-red. The principles of operation of this type of spectrometer are now well known (see Ref. [9]) but the advantages and disadvantages are still being argued. The most obvious advantage in the very-far infra-red is that all the wanted energy corresponding to a given spectral range falls on the detector at any one time, while for the conventional spectrometer only that corresponding to a narrow spectral range does so. This creates a much greater signal-to-noise ratio but it is not immediately obvious that this is an advantage in ultimate resolution. It may be shown that there is considerable advantage when the ultimate sensitivity of the detector is not limited by background radiation but by such things as current noise. For detectors in general use, the latter condition normally holds (see Refs. [9], [14]). From 300 μm–1000 μm the advantage is with the Fourier transform type but for shorter wavelengths this is not generally agreed as being so (see Ref. [13]).

By use of a lamellar type of grating RICHARDS [14] has been able to design a very compact vacuum instrument, which is shown diagrammatically in Figure 2. With this instrument RICHARDS has been able to work out to a wavelength of 3000 μm and has obtained a resolution of 0.05 cm^{-1} at 200 μm and 0.1 cm^{-1} at the long-wave end of the useful range of the instrument. Various commercial designs of transform spectrometers are now available. Experience with the use of these is discussed in Refs. [36] and [38]. They have been most useful in improving resolution of line spectra or indeed of any spectra with rapid variations of intensity. Some difficulties have been experienced in determining relative intensities of widely separated groups of lines and in the measurement of absolute values of absorption. Related to these difficulties is that of obtaining accurately the absorption coefficient when this varies slowly with wavelength.

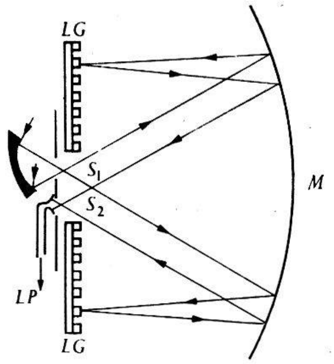

Figure 2

Fourier-transform spectrometer using a lamellar grating for the very-far infra-red (after RICHARDS [14]). S_1, entrance slit; S_2, exit slit; LP, light-pipe; LG, lamellar grating; M, paraboloidal mirror.

The disadvantage of not being able to see the spectrum as it is being taken is being overcome through the use of on-line electronic digital computers in conjunction with the spectrometer to give immediately the Fourier transform of the observed 'signal' i.e. the real spectrum as a function of wavelength. This adds considerably to the complexity of the equipment unless a large computer is available on a time-sharing basis.

6. Detectors for Very-far Infra-red

One of the most remarkable developments in infra-red techniques which has taken place in the past decade has been the extension of photoelectric detection methods with their great advantages of combined speed and sensitivity, to the far and very-far infra-red. Photoelectric detectors for the infra-red have been mainly of the photoconductive type. For the intermediate infra-red region of the spectrum, 'intrinsic' detectors based on PbS, PbSe, PbTe, InSb, etc. have been widely used and for the far infra-red (15–100 μm) 'extrinsic' detectors based on Ge have extended the wavelength range available to photoelectric detection by more than a decade. The longest wavelengths at which such detectors are useful is about 120 μm. For example FRAY and Oliver [15] have described a Ge detector using In as dopant, while more recently B has been used as a dopant for the same wavelength range [16].

These detectors cover only a very small part of the very-far infra-red and it seemed unlikely that this kind of detector would operate at much longer wavelengths. However, the discovery of two new phenomena associated with very shallow donors in InSb led to fast photoelectric detectors with a range extending well beyond the conventional limit (1000 μm) of the very-far infra-red. The first of these phenomena is the freezing of electrons into very shallow donors in a magnetic field and was successfully used by Putley [17], to make a very fast and sensitive detector for the range 500–2000 μm. By using a higher magnetic field a more peaked response may be obtained and, by varying the magnetic field, a tunable detector may be obtained. Such a detector has been described by Kimmitt and Niblett [18]. These detectors operate at liquid helium temperatures, have time constants in the range 10^{-7}–10^{-8} sec. and a noise equivalent power of the order of a few times 10^{-12} W/(Hz)$^{1/2}$ when used with the best available amplifiers. It is of interest to note that the ultimate sensitivity which can be achieved at present is set by noise in the first stage of the amplifier.

The second new phenomenon leading to fast detection in the very-far infra-red is the 'electron bolometer' effect. This occurs in semiconductors such as InSb with a very high electron mobility at low temperature. The incident radiation heats the conduction electrons, which are loosely coupled to the lattice, changing their mobility but not their concentration to any extent. The time-constant is determined by the electron-lattice relaxation time and is also in the range 10^{-7}–10^{-8} sec. This form of photoconduction has been studied by Rollin [19] and Kogan [20] and has been used by Kinch and Rollin [21] to make a sensitive detector for the very-far infra-red without the use of a magnetic field. In this case a step-up transformer, which must operate at liquid helium temperature, is required to raise the impedance of the detector element so as to match the input of the first stage of the associated amplifier. Commercial versions of this type of detector and also of that described by Putley [17] are now available.

These photoelectric detectors have given a strong impetus to the development of techniques for the very-far infra-red. When, as frequently occurs, short-lived phenomena are being observed their use is essential. For many uses in spectroscopy, however, the shorttime-constant, which is characteristic of these photoelectric detectors is unnecessary and one can now obtain about the same ultimate sensitivity over a much greater spectral range with thermal detectors having much longer time-constants. To obtain the highest available sensitivity the modern tendency is to use bolometers cooled to liquid helium temperature. The simplest of these is the carbon-flake bolometer but this suffers from excessive current noise. The most sensitive is probably the superconducting bolometer originally developed by Andrews and his colleagues for use at liquid hydrogen temperatures (see Ref. [9]) but more recently adapted for use at liquid helium temperature by Martin and Bloor [22]. The necessity for maintaining the temperature of the liquid helium bath very steady, so as to keep the sensitive element at a fixed point on the superconducting transition, leads to a rather complex equipment and the system has not been used to any great extent by other workers. A much simpler detector, which is almost as sensitive, is the single-crystal germanium bolometer first introduced by Low [23] and further developed by Low and Hoffman [24]. This type of bolometer has now largely replaced other detectors when the highest sensitivity is required over a large spectral range in the very-far infra-red, and particularly when a uniform response is a great advantage as for Fourier-transform spectroscopy.

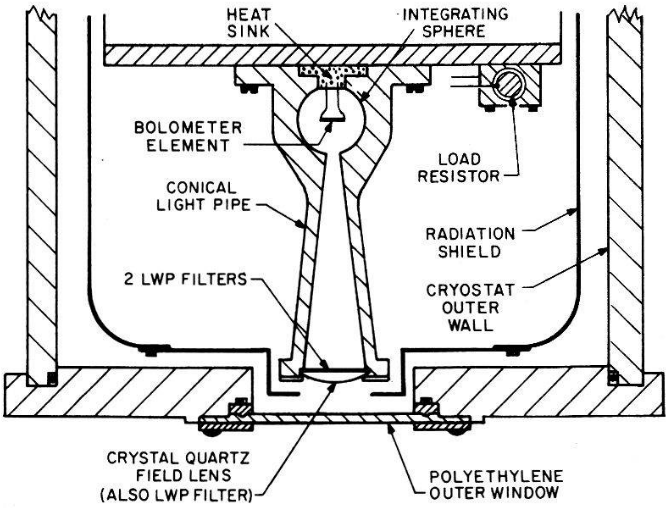

Figure 3

Optical system for fast germanium bolometer (after Zwerdling, Smith and Theriault [26]).

The commercial detectors of this type which are readily available are quite slow in response and lose a good deal of their sensitivity if operated at frequencies much in excess of 20 Hz. This is somewhat low for many applications and leads to trouble with low-frequency noise in amplifiers and with the increased noise at low frequencies due to the exciting current. It is frequently desirable to operate at frequencies of a few hundred Hz while retaining a noise equivalent power of at least 5×10^{-12} W/(Hz)$^{1/2}$. The difficulty is that to obtain a short time-constant a thin flake of material must be used for the bolometer element and this reduces the absorption of the incident radiation to an intolerable extent unless special arrangements are made. The addition of absorbing blacks similarly increases the time-constant. The author and his former colleagues at the Massachusetts Institute of Technology have made a very detailed study of the single crystal bolometer and have developed a detector with a noise equivalent power of about 4×10^{-12} W/(Hz)$^{1/2}$ for the 'chopping' frequency range 200–1000 Hz. This will be described briefly in the next section.

7. A Fast, High-responsivity Germanium Bolometer

The use of a single crystal for the bolometer element greatly reduces current noise as shown by Low [23]. A thin element is necessary in order to keep down the thermal capacity and low temperatures must be used to take advantage of the rapid decrease of specific heat at such temperatures. This also has the further advantage of reducing the random thermal fluctuations in the element (see Ref. [9]). In order to obtain adequate optical absorption in the element use is made of the high absorption coefficient observed in p-type compensated Ge by Smith *et al.* [25]. This material with suitable concentrations of dopants has also a fairly high value of the temperature coefficient of resistance – a desirable feature for a bolometer element (see Ref. [9]).

The absorption of incident radiation in the element is further increased by use of a special optical arrangement involving a light-pipe and integrating sphere, shown in Figure 3. The bolometer has been described together with detailed measurements of its electrical and thermal parameters by ZWERDLING, SMITH and THERIAULT [26].

The sensitive element consists of part of a specially grown single crystal of Ge having a concentration of Ga acceptors equal to 9×10^{15} cm^{-3} and a concentration of Sb donors equal to 1×10^{15} cm^{-3} so that the compensation ratio K is equal to 0.11. The element is supported by two thin copper leads attached to the smallest ends. These serve the dual purpose of providing electrical connections and also contribute a large part of the thermal connection to the heat sink. The leads are 0.125 mm in diameter and are coated with a tough polyester film having a thickness of approximately 12 μm. The element is mounted with its largest faces normal to the axis of the light pipe (see Figure 3).

The fraction of radiant power in a parallel beam, incident normally on the element and absorbed by it, is shown in Figure 4 as a function of the wavelength λ. An experimental determination of the effective emissivity of the bolometer gives the fraction of power incident on the outer aperture of the light pipe which is absorbed in the element. This is about 0.51 and varies very little with wavelength.

The equivalent noise power of the bolometer element is about 2×10^{-12} W/(Hz)$^{1/2}$ and when account is taken of the effective emissivity the equivalent noise power of the bolometer system is approximately 4×10^{-12} W/(Hz)$^{1/2}$ when operated at frequencies between 200 Hz and 1000 Hz, and at a temperature of 1.55 °K. This includes the noise due to a special pre-amplifier designed by ZWERDLING, THERIAULT and REICHARD [27]. Thus we see that a bolometer capable of operating at frequencies up

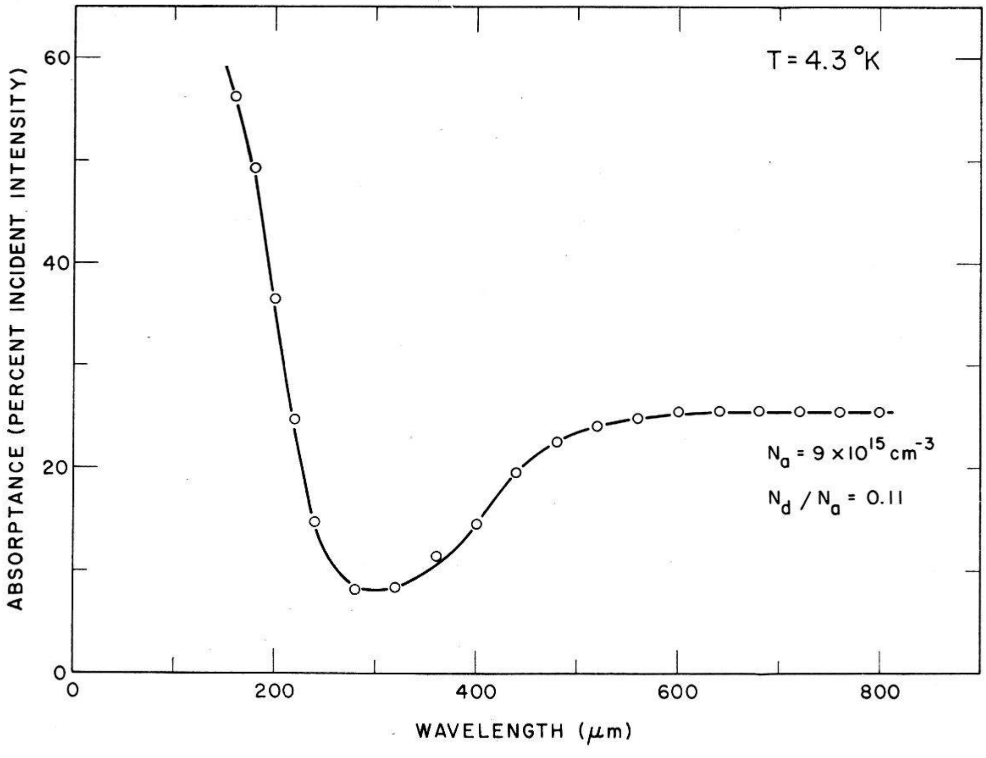

Figure 4

Fraction of radiant power in parallel beam at normal incidence absorbed by bolometer element.

to 1 kHz without much loss in ultimate sensitivity can be made using these techniques. For operation at higher frequencies the ultimate sensitivity falls off, corresponding to a time constant of the order of 260 μs. It was found that there was a considerable advantage to be gained in operating the bolometer at 1.55 °K, the lowest temperature conveniently available with the cryostat in which it was mounted. DREW and SIEVERS have used a single-crystal Ge bolometer having a somewhat longer time-constant, at a temperature of 0.4 °K obtained with He^3 (see Ref. [46]).

8. Novel Detection Methods

The methods of detection discussed above, apart from the 'electron bolometer', are extensions of techniques already used at shorter wavelengths. We now shall discuss briefly two techniques which are now being developed. The first is quite new and the second is an extension of a technique used for microwaves.

The first technique depends on the observation of the effect of very-far infra-red radiation on point-contact superconducting junctions of the kind described by JOSEPHSON [28]. This effect, which shows a modulation of junction current by the incident radiation, seems to have the possibility of providing a fast, sensitive detector. It has been described by GRIMES, RICHARDS and SHAPIRO [29]. The second technique consists of mixing of the incident radiation with the output of a laser which acts as a local oscillator, and is simply an extension of the heterodyne method used in radio and microwave techniques. Now that a number of frequencies are available for the local oscillator (see Section 3) a wide range of wavelengths in the very-far infra-red is accessible to this technique. The main problem is to find an efficient mixer. Various crystal materials have been used; for example ZERNIKE and BERMAN [30] used quartz, while YAJIMA and INOUE [31] used ZnTe. A new technique which uses a very fine wire in light contact with a metal surface (usually silver or steel) has been developed by JAVAN [32] and his colleagues. This shows promise of providing a more efficient mixer which should enable the technique to be exploited with very large gain in available sensitivity; it should be possible to decrease by several orders of magnitude the minimum power detectable if current noise in the mixer can be eliminated. Such techniques will undoubtedly play a large part in further opening up this region of the spectrum in the future.

9. Some Physical Investigations in the Very-far Infra-red

We turn now to examine some of the recent achievements in physics research brought about principally through the development of the techniques we have been describing. The subject is now a wide one with an extensive literature and in the space available it is possible to select only one or two topics for discussion.

Molecular spectroscopy has been carried out for some time in this region of the spectrum; for example the strong water-vapour bands, which are so troublesome in other investigations, have been extensively studied. With the improvement of techniques many other molecules have been investigated.

It is perhaps in the study of solids that spectroscopy in the very-far infra-red has led to the most interesting and surprising new results. For example the absorption spectra of atoms and small molecules trapped in the cage-like structures of clathrates occur in the very-far infra-red and these have been studied by a number of workers. For example Burgiel, Meyer and Richards [33] observed absorption spectra in the wavelength range 120–730 μm due to Ar, K, Xe, CO and O_2 in β-quinol clathrates. It is an intriguing picture to visualise these atoms and molecules dashing about like trapped animals in a cage and being stimulated to higher activity by the incident radiation!

Naturally the *reststrahlen* absorption, particularly of the alkali halides has been studied in greater detail for example, by Jones and his colleagues [34]. Various other optical materials such as the fluorides of Ca, Sr, Ba and Cd have been studied by Bosomworth [35]. These are interesting in showing clearly two-phonon processes which are difficult to observe in the alkali halides. The absorption spectra of solids containing heavy ion groups occur in the very-far infra-red and some have now been studied. For example, spectra of alkali salts of platinum halide complexes have been examined by Perry and his colleagues [36].

Spectra due to certain impurities in alkali halides surprisingly appear in the very-far infra-red. For example the light atom Li gives rise to long-wave absorption peaks in KBr. By use of the isotopes Li^6 and Li^7, Sievers and Takeno [37] have definitely identified the absorption peaks at 558 μm and 613 μm as being respectively due to the lighter and heavier isotopes, and have proposed theoretical explanations for the absorption at these long wavelengths.

Rare earth ions in various crystals have been a fruitful source of spectra in the very-far infra-red. For example Hill and Wheeler [38] have investigated the transitions between levels due to Er, Dy, and Sm in their ethyl sulphates due to Stark and Zeeman splitting.

An interesting investigation of the absorption of both normal and heavy water (H_2O and D_2O) has been made by Draegert *et al.* [39] in the range 10–330 μm, while various non-polar liquids have been studied by Chantry *et al.* [40].

Some of the most interesting new kinds of spectra for this region have been associated with magnetic phenomena. For example Richards [41] observed strong absorption in the antiferromagnet NiF_2 at 3000 μm and 322 μm with no magnetic field and studied the variation of the position of the absorption lines with applied magnetic field. Burgiel and Hebel [42] found several absorption lines in Bi in a magnetic field in the range 118–770 μm. These are attributed to combined spin and cyclotron resonances arising from the conduction electrons in the rather complex band structure of Bi.

10. The Forbidden-energy Gap in Superconductors

One of the oustanding contributions of spectroscopy in the very-far infra-red has been the very direct evidence it provided for a forbidden energy gap in superconductors. Even before the current theory (BCS) of superconductors due to Bardeen, Cooper and Schrieffer [43] there had been a good deal of evidence suggesting the existence of a forbidden energy gap separating the electronic states corresponding to the superconducting and normal conditions of a metal. By measuring the energy loss on reflection in the very-far infra-red for a number of superconductors Richards and Tinkham [44] provided direct experimental evidence for an energy gap 2Δ and confirmed the order of magnitude predicted by the BCS theory, namely $3.5\,k\,T_c$ (for values of temperature T considerably less than T_c) where T_c is the critical temperature. For frequencies such that $\hbar\,\omega > 2\Delta$ the loss due to optical absorption in the superconducting metal is virtually the same as for a normal metal but when $\hbar\,\omega < 2\Delta$ the absorption decreases rapidly indicating the presence of an energy gap.

This technique has since been used by a number of workers to obtain values of Δ for most known superconductors. (Values of Δ have also been obtained from electron tunnelling across superconducting junctions.) It has been used recently by CAPPELETTI, GINSBERG and HULM [45] to determine the forbidden energy gap for alloys in the system Zr–Nb–Mo which behave in some interesting ways differently from simple superconducting metals.

A new and interesting technique for measuring the absorption in superconductors has been reported by DREW and SIEVERS [46]. A thin metal foil is rolled up with a thin polyethylene sheet into the form of a 'jelly roll' and inserted in a light-pipe which can be cooled. The radiation passes through the roll as through a strip wave-guide for which the losses can be calculated fairly exactly. In this way the absorption coefficient is obtained.

11. Impurity-band Conduction in Compensated Semiconductors

Superconductivity was undoubtedly the most important transport phenomenon which, until the advent of the BCS theory, had no adequate theoretical explanation. Indeed there are still some aspects of it that are not completely understood. There are, however, other transport phenomena which also set theoretical problems. One of the most interesting of these is the so-called impurity-band conduction in semiconductors. This has received a great deal of both theoretical and experimental attention in recent years. The phenomenon occurs in compensated semiconductors for which the conductivity does not become very small at low temperatures, as would be expected if the carriers were frozen into impurities having a finite ionization energy. The existence of unfilled as well as filled donors or acceptors in compensated material allows a 'hopping' type of conduction to take place. This has been studied from dc to microwave frequencies but there is a need for information on the behaviour of the electrical conductivity at even higher frequencies, namely those corresponding to the very-far infra-red. For frequencies higher than about 200 μ, excitation and ionization of simple donors or acceptors obscures the phenomenon in Ge and the range of wavelengths for which useful data is likely to be obtained is about 200–2000 μm. A theoretical treatment for this range has recently been given by BLINOWSKI and MYCIELSKI [47]. Experimental data for compensated Si obtained by NEURINGER, MILWARD and AGGARWAL [48] using a Grubb-Parsons Fourier-transform spectrometer gives remarkable agreement with the theory. Measurements for compensated p-type Ge by SMITH *et al.* [25] using a Perkin Elmer grating spectrometer, on the other hand, gives an absorption coefficient which is considerably higher and varies less rapidly with wavelength than is predicted by the theory. The latter has been given for n-type material but the behaviour of p-type would be excepted to be similar. The results of NEURINGER, MILWARD and AGGARWAL for Si are shown in Figure 5 and those of SMITH *et al.* in Figure 6. Some of the compensated Ge used for these measurements was also used for the bolometer elements described in Section 7.

The electrical conductivity σ cannot, of course, be measured directly at these very high frequencies but may be obtained from the absorption coefficient α by multiplying by an appropriate constant. (For Ge $\alpha \simeq 100\,\sigma$ [49].) In this relationship the conductivity is given at the angular frequency ω. For compensated material the conductivity at frequencies between 200 μm and 1000 μm is much higher than the dc conductivity. While the latter varies exponentially with reciprocal temperature, at low temperatures, the conductivity in the very-far infra-red hardly varies at all between 4.2 °K and 1.7 °K.

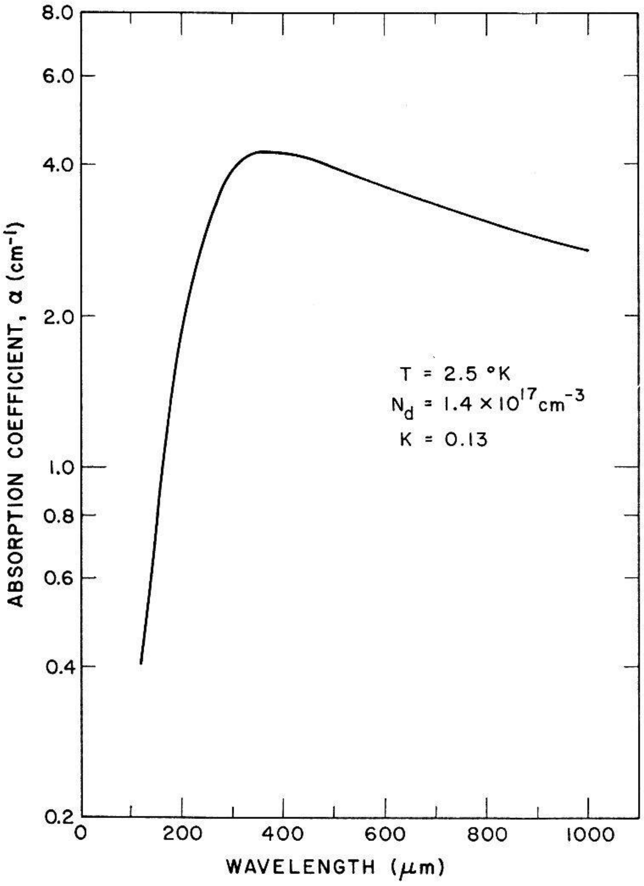

Figure 5

Absorption coefficient α for compensated *n*-type Si in the very-far infra-red (after NEURINGER, MILWARD and AGGARWAL [48]).

From Figure 6 it will be seen that the absorption falls rapidly when the wavelength becomes greater than 200 μ. The absorption at shorter wavelengths is due to excitation and ionization of single donors and acceptors and is not of interest in the present context. It is with longer wavelengths that we are concerned. According to the theory of Blinowski and Mycielski this absorption in n-type material is due to pairs of donors – one occupied by an electron and one empty – in the field of a charged acceptor. The 'hopping' conduction is induced by absorption of a quantum of the incident radiation. For p-type material the roles of donors and acceptors would be reversed. The discrepancy between the predicted and observed values of the absorption in p-type Ge has not yet been accounted for.

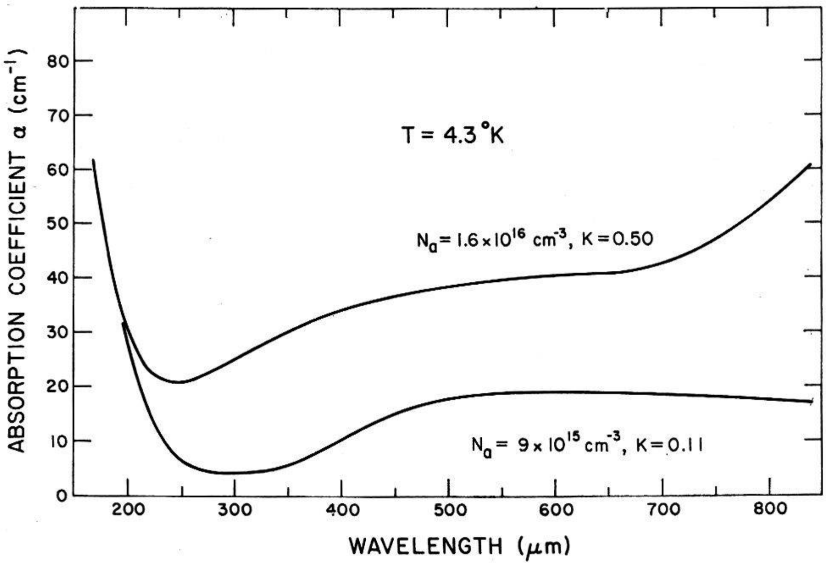

Figure 6

Absorption coefficient α of compensated *p*-type Ge in the very-far infra-red (after SMITH *et al.* [25]).

For uncompensated Ge the conductivity and also the absorption coefficient become very small at liquid helium temperatures. At higher temperatures where conductivity is due to free electrons or holes the constant ratio of absorption coefficient to conductivity has been shown by GIBSON [50] to hold up to microwave frequencies. For this material preliminary experiments appear to indicate that the absorption coefficient in the very-far infra-red is *less* than would be given by the dc value of the conductivity.

12. Conclusions

It will be seen that many interesting phenomena have been studied using techniques developed for the investigation of the very-far infra-red region of the spectrum and those we have discussed form only a representative sample. Many of the materials studied by Professor G. BUSCH in his long and active career as a physicist have played a part in these developments. Although this has not been one of the many research activities in which he has participated, it is one that has blossomed and borne fruit during his professional life as a physicist and has provided 'feed-back' into many other areas of physics research. Like him, it is clearly also one that is still active and may bring forth new and surprising results.

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