

The**SPEX****INDUSTRIES, INC. · 3880 PARK AVENUE · METUCHEN, N. J., 08840 · ☎ (201) 549-7144****Speaker****A BUILDING BLOCK APPROACH TO SOLID STATE SPECTROSCOPY****James Ferguson****Research School of Chemistry, Australian National University, Canberra, Australia**

OUR technical civilization today is a direct outgrowth of man's curiosity about the chemical elements and their compounds. Whereas chemistry, through chemical innovation, has led during the past century to the synthesis of a multitude of compounds and materials serving mankind in uncountable ways, it is only in the past decade or two that physics, by uncovering the properties of solid state materials, has played a leading role in our life style. While not yet household words, GaP light emitting diodes, silicon transistors and integrated circuits, yttrium aluminum garnet gems, selenium copying drums, and rare-earth-activated YVO₃ phosphors in TV screens have become items of every-day living. These practical physical properties of solid state materials are the dividends of fundamental research into solid-state physics.

In contrast to the vast majority of chemically important compounds for which the atomic structure is the crucial property, the significant characteristics of solid-state materials are associated with the electrons and not the atoms directly. Atoms, of course, are the essential constituents of solid-state devices, but their main role lies in providing a framework for the electrons.

Electrons carry a negative charge and they respond to an electric field. They also have a property called spin; they therefore possess a magnetic moment, so they respond to a magnetic field. Interactions between electrons and electric and magnetic fields establish basic characteristics of the majority of solid-state devices, and much fundamental research has aimed at understanding these interactions. One particular type of electromagnetic interaction involves light because light is characterized by transverse, oscillating electric and magnetic field intensities. The study of the interactions between light and the electrons in a solid is a branch of spectroscopy dealing with the electronic structure of the material in ground and excited states. The latter are reached by absorption of light energy, corresponding to electron jumps from one orbital to another higher orbital, while the return downward jump or fall causes the emission of light, which is luminescence.

Fundamental understanding of the electronic structure of chemical molecules has been gleaned through spectroscopic study of the absorption and emission of light by molecules in the vapor phase, mainly at room temperature. In order to obtain analogous data about the electronic structure of solids, however, it is necessary to quell the thermal motion of the atoms by cooling to temperatures close to absolute zero. Much of the contemporary surge in solid state spectroscopy springs from the widespread availability of liquid helium at reasonable prices.

One immediate result of the interaction between light and the electrons in a solid is the reduction of the velocity of light below the vacuum value; the ratio of the latter to the value in the solid is, of course, the refractive index. Before evaluating refractive index as a structural probe, we should consider more carefully the atomic arrangement of the solid and distinguish glassy and amorphous solids from crystalline materials.

A crystal can be considered to be composed of a single unit, the primitive cell, which is repeated in three dimensions by simple translations along the three cell axes. The arrangement of the atoms in the primitive cell determines its symmetry and the number of refractive indices which the crystal exhibits. There are seven crystal systems: cubic or isometric (isotropic); trigonal, hexagonal, and tetragonal (uniaxial); orthorhombic, monoclinic, and triclinic (biaxial). Only the cubic system behaves as an isotropic medium for the propagation of light, one where refractive index is independent of both the plane of polarization of the light wave and the direction of propagation. The propagation of light in the other six crystal systems is characterized by either two or three different refractive indices, corresponding to one optic axis (uniaxial) or two optic axes (biaxial), respectively.

Since uniaxial and biaxial crystals are optically anisotropic, it is necessary to define the plane of polarization of the light with respect to the principal refractive index directions in the crystal in order to carry out meaningful measurements. If the crystal absorbs light, then the intensity of the absorption is also anisotropic and varies with the plane of polarization. For all but monoclinic and triclinic crystals the principal absorption directions coincide with the principal refractive index directions; this is a requirement imposed by the symmetry of the crystal lattice. In practice these two sets of directions usually coincide for monoclinic and triclinic crystals, also, unless the absorption intensity is extremely high. When it is we must consider the refractive index to be a complex quantity whose real part is the refractive index and imaginary part is the absorption index. Detailed analysis of such a situation becomes very complicated and is beyond the scope of this article.

The variation of absorption intensity with direction of polarization of the light is termed linear dichroism (LD). For uniaxial crystals LD refers to the difference in absorption of light polarized in a plane parallel to the optic axis (π) and perpendicular to this axis (σ). For biaxial crystals LD is more complicated; absorption intensities must be measured for polarization planes parallel to each of the three principal refractive index directions. There are associated problems of crystal cutting and polishing required to get crystal sections containing these directions.

So far we have considered only the phenomenon of linear dichroism. However, it is also possible to obtain meaningful results with circularly polarized light (a special case of elliptical polarization). Circularly polarized light can be considered to be composed of two plane polarized rays, of the same wavelength, but vibrating in planes perpendicular to each other, and with a phase difference or relative retardation of one quarter of the wavelength. The plane of polarization then rotates either clockwise or counterclockwise. Circularly polarized light can propagate along any direction in cubic crystals and along the optic axis of uniaxial crystals.

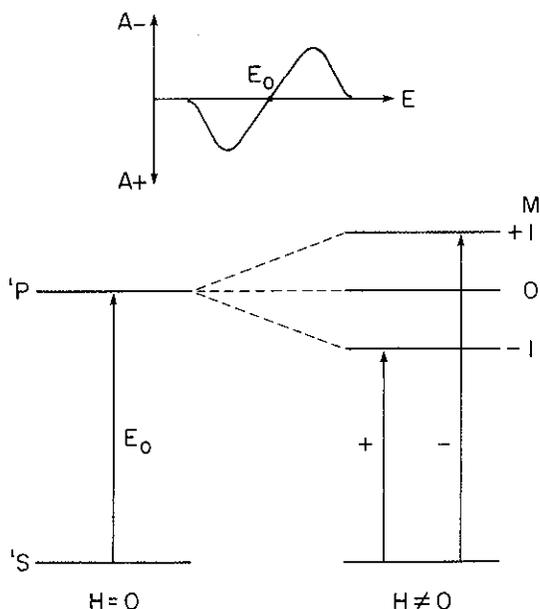


Fig 1 Energy levels for $1S$ and $1P$ states with and without an applied magnetic field together with the circularly polarized transitions for the latter. The form of the MCD curve is shown in the upper part.

In some cases the absorption intensity for left circularly polarized light differs from that for right circularly polarized light. This difference is called circular dichroism (CD), and it can occur for naturally optically active molecules and crystals as well as for materials placed in an external magnetic field where the circularly polarized light propagates along the field direction; the latter case we refer to as magnetic circular dichroism (MCD). The magnetic field removes the degeneracy of electronic states through differing magnetic interactions. The simplest way to see how the MCD arises is to consider an electronic transition between S and P states as shown in Fig 1. The MCD signal (i.e., the difference between the absorption intensities of left and right circularly polarized light) then has a differential shape, also shown in Fig 1, the so-called A term. (The reader is referred to a review by P.J. Stephens [1] for more detailed theoretical discussions of MCD.)

In order to uncover the electronic structures of crystals through optical spectroscopy, it is necessary to experiment with single crystals cooled to very low temperatures and probed with linearly polarized light (except for cubic crystals) or circularly polarized light (cubic and uniaxial crystals). Measurements can be made either of absorption or emission of light. Solid state spectroscopic research therefore requires an impressive array of specialized instruments if advantage is to be taken of all the available techniques. In these days of smaller research grants and higher inflation, cost compromises reduce the number of affordable options below what one would wish.

Clearly, a building block approach gives greater flexibility to a research program, assuming that components can be rearranged simply and quickly for the necessary range of techniques. This is the approach adopted in our laboratory, and the present article reviews some of our developments. Our basic difficulty is geographical, Australia lying far removed from those countries where we must purchase our blocks. This isolation leads naturally to a spirit of do-it-yourselfness which adds an ingredient of flexibility. This spirit is shared by a number of talented technical experts who have put academic ideas into practice.

The most important building block is, of course, the spectrometer, which must be as flexible as possible. Fortunately, Spex Industries has recognized the advantages of flexibility, and their spectrometers provide, in the opinion of the author, the most convenient design features for modular systems. Three Spex spectrometers are currently operating in the author's laboratory: a ten year old $3/4$ m model is the work horse for a variety of luminescence studies; more recent 1704 and 1402 models are primarily dedicated to the solid-state program. The latter two spectrometers—a single and a double—allow a variety of measurement techniques, and this article describes a number of those techniques. The prime consideration in nearly every case has been developing the technique in a way which enables us to study small single crystals so that sample size is not a limiting factor.

The 1704 spectrometer was chosen for measurements of linear dichroism and magnetic circular dichroism. As mentioned above, both LD and CD embody differences of absorption (or emission) intensity between two senses of polarization. Measurements can be carried out by comparing the spectra for the different polarization planes, a procedure that is satisfactory when the differences are large. With small differences a modulation technique is more suitable. All instruments which measure CD now resort to the latter, a method involving the generation of an alternating birefringence in an otherwise isotropic material. Initially this was achieved with a Pockel's cell, a single crystal of KH_2PO_4 or a related material cut so that the light beam travels along the optic axis of the uniaxial crystal. This crystal can be made anisotropic (or birefringent) by applying a voltage between the two faces to obtain $\lambda/4$ retardation. Unfortunately, the crystals are expensive, fragile, and susceptible to damage by atmospheric moisture.

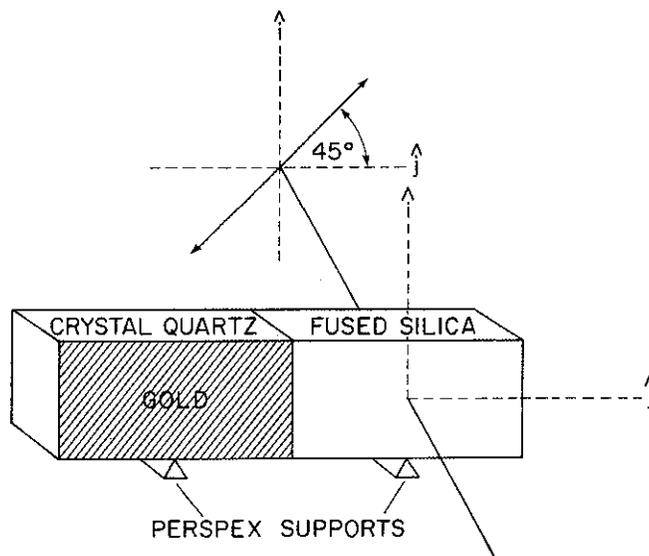


Fig 2 Photoelastic modulator (after Jasperson and Schnatterly[2]).

More recently, the birefringence has been achieved by means of a photoelastic modulator which can be very easily adapted for either CD or LD measurements. This device was described by Jaspers and Schnatterly [2] and by Kemp [3], and its essential features are shown in Fig 2. It consists of a single quartz crystal with a -18° x-cut and gold electrodes evaporated on the two main faces. This crystal can be made to oscillate by applying a sinusoidal voltage of a few volts, at a frequency of about 50 kHz, along the long axis of the crystal. A piece of isotropic fused silica, cut so as to have the same resonant frequency as the crystal oscillator, is cemented to it. When the oscillator is driven the fused silica part becomes birefringent by an amount directly proportional to the magnitude of the strain. Adjustment of the driver voltage (on the order of 10-20 V) can easily be made to give either $\lambda/2$ or $\lambda/4$ retardation. These retardations can be achieved throughout the ultraviolet, visible, and near infrared regions with silica, in contrast to the Pockel's cell which cannot be used in the near infrared region.

The optical arrangement is the same for measurement of LD or CD. For absorption measurements a monochromator provides monochromatic light. A polarizer is set at 45° to the modulator axis (see Fig 2), and the sample is placed between the modulator and the photodetector. Phase-sensitive (lock-in) detection then directly yields the differential absorption. For CD this is detected at the oscillator frequency and for LD at twice this frequency. Differential absorption permits detection of differences in absorbance as small as 1×10^{-5} . In order to measure MCD an axial magnetic field is applied to the sample; a schematic of the overall arrangement is shown in Fig 3.

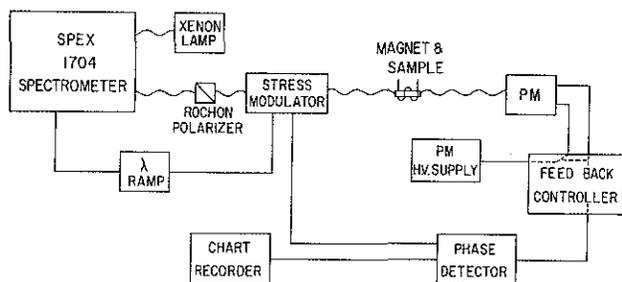


Fig 3 Schematic of the magnetic circular dichroism spectrometer.

There are three ways of obtaining a suitable magnetic field: with a permanent magnet, an electromagnet, or a superconducting solenoid. We find that the first and the last complement each other nicely. The inexpensive permanent magnet (0.5 T; 1 tesla = 10^4 gauss) has a small-diameter hole drilled through the pole pieces so the light can propagate in the field direction. The sample is cooled by boil-off from a liquid helium storage container through a silica tube in its neck (see Fig 4). The pole gap is 14.5 mm, and the flow tube has a square cross-section piece, strain free, which fits in this gap. Variation in sample temperature is easily achieved by controlling boil-off of the liquid helium. The advantages of the flow tube plus permanent magnet technique lie in the ease with which an experiment can be completed at short notice, the ease of temperature variation, and the ability to change samples in a few minutes—thus preliminary scanning of a number of samples can be carried out quickly in order to find one most suitable for detailed study. This preliminary scanning is often necessary because of the effects of strain. Strain induces birefringence and therefore spurious dichroism. Disadvantages are the relatively low magnetic fields and the small light flux. Both of these variables are related to the overall performance. The magnetic field splitting of the lines is clearly dependent on the field strength, while the limiting factor in the photomultiplier signal is the shot noise, so that high light flux is

important. Our superconducting solenoid allows variable fields up to 5T, and it has been designed to provide high light flux.

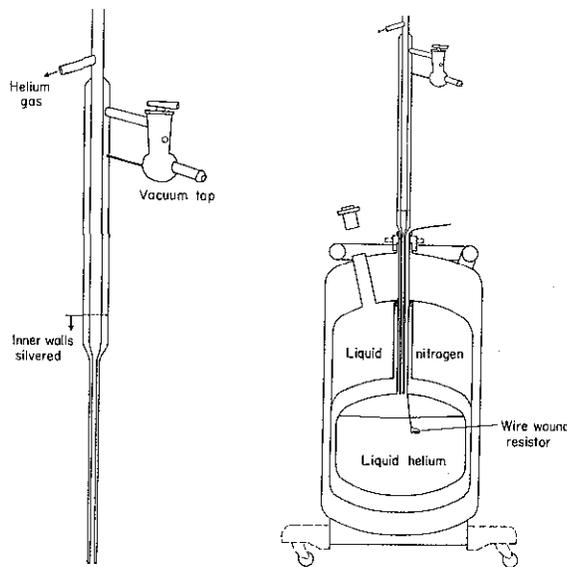


Fig 4 Typical cryogenic flow tube. Liquid helium is heated to the gas which is then driven through the silica tube.

In exploiting both MCD and LD fully one should not be limited by resolution as lines as narrow as about 0.01 nm often need close examination. No commercial circular dichrograph provides this resolution as yet. Light flux then becomes a critical factor, so a monochromator with large aperture is needed, with the largest slit height compatible with other optical constraints. The 1704 with curved slits satisfies these requirements. A re-transmitting potentiometer attached to the scanning mechanism furnishes a signal proportional to wavelength for driving the modulator at constant retardation. Also, by selecting a 2400 grooves/mm grating we have been able to resolve any spectral features of interest so far. To illustrate the resolution of this system we discuss briefly the MCD associated with a sharp line in the absorption spectrum of RbMnF_3 , a cubic antiferromagnet.

The primitive cell of RbMnF_3 is a cube with the manganese atom at its center and a fluorine atom at the center of each of its six faces (Fig 5). Because of its electronic structure, each Mn has

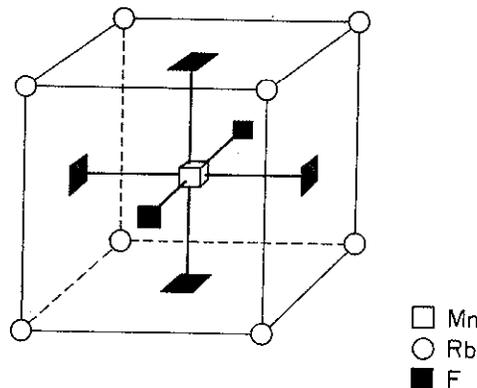


Fig 5 Perovskite fluoride cubic cell.

a magnetic moment, and at low temperature these moments adopt an ordered array such that each cell has its moment exactly anti-parallel to those of its six neighbor cells. The crystal lattice is then composed of two sets of cells, the magnetic moments of one set being opposed to the moments in the other set, so there are two equal and opposite magnetic sub-lattices. Although this is a common property of all antiferromagnetic crystals, very few have the high symmetry which makes RbMnF_3 an attractive model for theoretical study. If we place the crystal in an external magnetic field whose orientation is not perpendicular to the direction of the internal sub-lattice magnetic moments, then the energy of the two sub-lattices is no longer the same, and two absorption lines will occur. The Zeeman splitting will have an associated CD, and it can be detected in the usual way. Unfortunately there is an additional complication with RbMnF_3 because an external magnetic field causes a rotation of the internal magnetic moments away from the applied field direction, with a resultant drop of signal. It is therefore necessary to conduct the measurements in weak fields. On the positive side, this situation highlights the capability of our apparatus. Fig 6 shows the MCD signal [4] associated with a narrow exciton line in RbMnF_3 , at 4.2°K , for external fields of 0.05, 0.15, and 0.25 T. The actual situation is a little more involved than that outlined above, the 0.25 T curve showing four lines, not two. This is explained as an additional degeneracy in the excited state which is removed by a complicated second order spin-orbit effect. However, the results clearly indicate the resolution and detection limits which can be achieved.

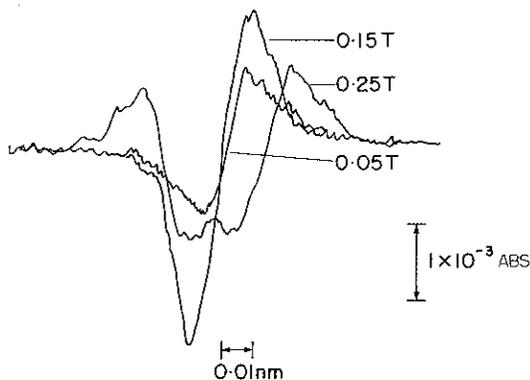


Fig 6 MCD signal associated with absorption to the $4E_g$ exciton state of Mn^{2+} at 4.2°K for three different applied magnetic fields parallel to (100).

The spectral range available with our system is greatly expanded with different gratings and detectors. A cooled (cold nitrogen gas) S-1 response photomultiplier, together with a grating blazed at 750 or 1000 nm, extends the range to about 1100 nm, and a cooled (liquid nitrogen) indium antimonide detector allows extension to about 2000 nm in air.

Another simple feature of our system is the monitoring of the photomultiplier voltage to obtain a measure of the absorbance. The electronic system includes a feed-back device (Fig 3) to maintain constant photo-current by changing the photomultiplier voltage. This change corresponds to a logarithmic change of light intensity, so it becomes a measure of the absorbance. It is fed into the second channel of a two-pen recorder to provide simultaneous MCD and absorption spectra.

The 1402 spectrometer was originally purchased for MCD measurements because of its low stray light. However, this property has proved to be far more desirable for solid state studies of absorption, fluorescence, and excitation as well as for photochemical studies. After trying a number of experimental

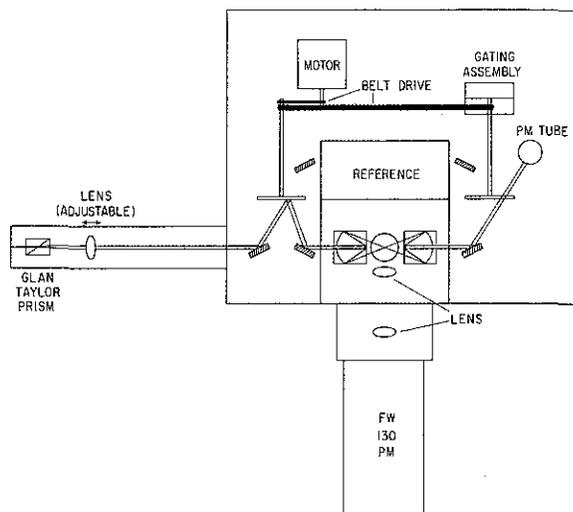


Fig 7 Diagram of double beam attachment.

arrangements we finally arrived at a multipurpose unit which enables us to carry out a variety of spectral studies of small single crystals with variable sample temperatures down to that of liquid helium.

This multipurpose unit is a double-beam attachment similar to the Varian Techtron 635 spectrophotometer. The optical section, which includes an adaptor tube containing a rotatable Glan-Taylor polarizing prism and focusing lens, attaches to the exit slit mounting of the 1402 spectrometer. This section contains sample and reference compartments, beam splitting mirrors, gating signal generators, and photomultiplier; it is diagrammed in Fig 7. The sample compartment was made large enough to hold two reflecting microscope objectives. Fig 8 is a top view of the attachment with the lid removed. The electronic processing and control sections are contained in a separate unit.

The double-beam system involves two rotating chopper wheels, each divided into three equal segments so that there are three distinct sequential photomultiplier signals: (i) Reference, (ii) Sample, and (iii) Dark. These waveforms are amplified by a preamplifier located near the base of the photomultiplier and then by the input amplifier in the control

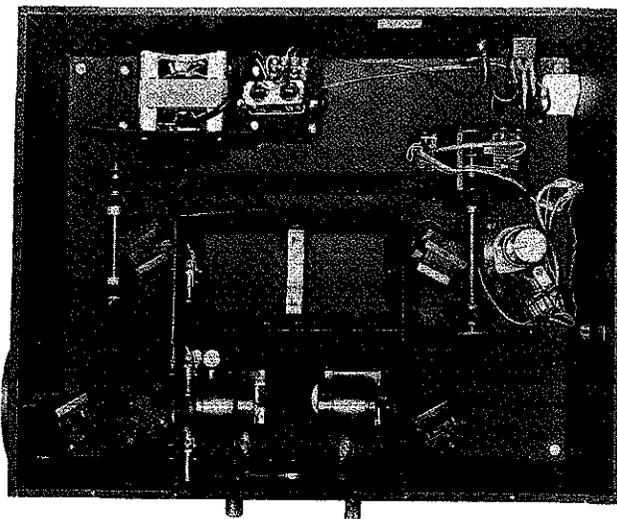


Fig 8 Top view of the double beam attachment with the cover removed.

section. The amplified signals are fed to three storage amplifiers (zero, signal, and reference) via three electronic switches synchronized with the optical beam choppers. Synchronizing pulses originate from a combination of one rotary disc and three fixed photoelectric trigger units. The disc is attached to the shaft of one of the chopper assemblies, and it rotates between the cell and lamp of each of the three equally spaced trigger units. The trigger signals are provided by G.E. type H131A1 units substituting light emitting diodes and phototransistors for the incandescent lamps in the Varian Techtron spectrophotometer.

The unit may be operated in either single beam or double beam mode with a percent transmittance and a number of absorbance ranges. The latter, as well as zero offset, are selected by push buttons.

An essential design feature of the attachment is the reflecting microscope objectives ($\times 15$) which allow measurements on crystals as small as 0.1 mm diameter. The relatively large working distance of these objectives accommodates a helium gas-flow tube (see Fig 4) for variable sample temperatures as low as about 5°K.

The attachment serves a variety of spectroscopic measurements: ground state absorption spectra, luminescence excitation spectra, excited state absorption spectra, luminescence emission spectra, and photochemical studies.

The first of these is a straightforward application of the double beam unit, while the others require additional detectors and/or light sources. However, each of these techniques can be performed without changing the position of the sample (or its temperature). Each of the measurements is described below.

Luminescence Excitation Spectra

Absorption of light creates an excited state which, because it is thermodynamically unstable, will decay either radiatively or non-radiatively. The former is called luminescence, and its intensity is proportional to the amount of light absorbed. It is possible in some circumstances to use the variation of the intensity of the luminescence, as the wavelength of the absorbed light is changed, as an approximation to the absorption spectrum. This can be easily seen from the fact that the measure of absorption intensity is the absorbance $Abs = \log(I_0/I)$ where I_0 and I are the incident and transmitted light intensities, respectively. Abs is approximately proportional to $I_0 - I$, the amount absorbed, if Abs is less than about 0.2. The technique is therefore mainly applicable to the detection of extremely small absorptions. Direct measurement is limited by light intensity fluctuations, so absorbances less than about 0.01 are difficult to measure, whereas the excitation technique is limited only by stray light.

The measurement of luminescence excitation spectra is also very convenient for two other situations which are discussed below. In the first, the method can discriminate between overlapping absorption bands due to different absorbing centers, only one of which emits light in a particular wavelength region. In the second, the method can evaluate the reflectivity of thin crystals in the region of strong absorption, where reflectivities can be very high.

The usual double beam method of determining absorption from the incident and transmitted light assumes that reflected light is identical for sample and reference beams. If, however, the reflectivity is appreciable, then the measured absorption is not the true absorption because part of the light has been reflected. Then it is more useful to consider the fractions of the incident light which are reflected (R), absorbed (A), and transmitted (T) by the crystal, thus, $1 = R + A + T$. Because $R \neq 0$ we

cannot obtain a measure of A from a measurement of T . The technique requires very pure monochromatic light as is characteristic of the 1402 double monochromator. The crystal absorbs light over a band of wavelengths ($\Delta\lambda_1$) and emits luminescence over another band of (longer) wavelengths ($\Delta\lambda_2$). If a photomultiplier, sensitive to $\Delta\lambda_2$, is used to detect the luminescence, then its signal will be proportional to the intensity of the absorbed light, provided we block off the exciting radiation ($\Delta\lambda_1$). This can be arranged by placing a sharp cut-off filter, which absorbs $\Delta\lambda_1$ and transmits $\Delta\lambda_2$, or an interference filter which transmits part of $\Delta\lambda_2$, between the sample and the photomultiplier tube. As we generally work with very small crystals we have selected an ITT FW 130 photomultiplier with a small photocathode; it is attached to the side-wall of the sample compartment of the double beam unit (see Fig 7). A small high-aperture lens is placed close to the flow tube to collect the luminescence. The signal can be amplified by dc, ac, or photon counting methods.

An outstanding feature of our arrangement is the ability to measure the luminescence excitation spectrum and either the transmission or the absorbance spectrum of the crystal simultaneously by means of a two-pen recorder. This duality of measurement is particularly valuable in determining the optical properties of very thin films of molecular crystals, which luminesce and also have high reflectivities. As an example of these systems a brief description of some recent work [5] on the optical properties of thin anthracene crystals is given here.

Anthracene has served as a convenient crystal to furnish experimental information for the development of theoretical models of excitons in molecular crystals. The exciton model, in this case, is the Frenkel type, and it describes the electronically excited state of the crystal in terms of properly constructed crystal functions of one excited molecule with the remaining molecules in their ground states. The essential feature of the model is the recognition that the electronic excitation energy is not localized on one molecule, but rather it can be considered as spreading out through the crystal away from the point of original absorption as a wave-like disturbance. The excitation energy is therefore treated as a quasi-particle called the exciton, and we have a wave-particle concept analogous to that which we are accustomed to associating with light (where the quasi-particle is called the photon). However, Hopfield [6] showed nearly 20 years ago that there is a coupling between the exciton and the photon such that a proper understanding of the optical properties of crystals in the region of the exciton band of energies requires consideration of this interaction. The coupled exciton-photon is usually called a polariton, sometimes a photo-exciton. The polariton model changes our concept of the energy states of an exciton, especially in relation to the mechanism of the actual absorption of energy from the light, and of the subsequent luminescence.

Although the polariton model has predicted behavior resulting from the interaction between light and molecular crystal, it is only recently that this behaviour has been observed experimentally [5], confirming the essential features of the polariton model. The important measurements for this confirmation involve the luminescence excitation spectrum and the transmission spectrum of a very thin anthracene flake, on the order of 50 molecules thick, held at a temperature near that of liquid helium. Under such conditions the fraction of the light actually absorbed (A) by the crystal is determined directly from the luminescence excitation spectrum, while the fraction transmitted (T) is given by the transmission spectrum, and the difference between unity and the sum of these two fractions gives the fraction of light reflected ($R = 1 - A - T$). Fig 9 shows the result of these measurements for a crystal 55 molecular layers thick [7]. The derived reflection spectrum has the same shape as that measured directly by Turlet and Philpott [8]. The

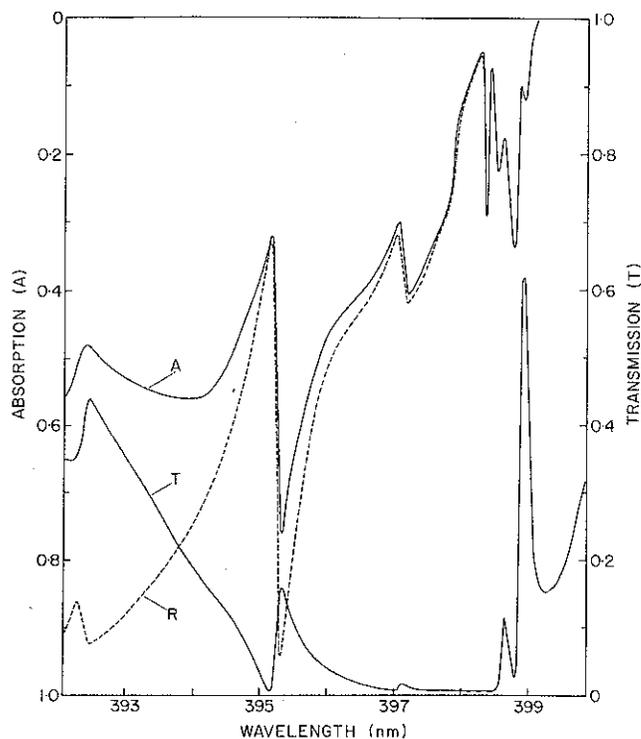


Fig 9 Transmission (T) and absorption (A) spectra of a thin anthracene crystal, 55 molecular layers thick, at 6.5°K, in the region of the *b* polarized exciton band. The reflection (R) spectrum was obtained from the relation $R = 1 - T - A$.

measurement of the excitation spectra of this crystal has another important aspect: it allows one to obtain a direct estimate of the effects of crystal inhomogeneities, such as strain due to mounting or the presence of deliberately added impurities. The polariton model predicts an increase of absorption by the exciton system, and this is confirmed by the experiments [7].

As another example of the power of the luminescence excitation technique let us consider the spectroscopic properties of crystals of KMgF_3 containing small amounts of Mn^{2+} . Although fluoride crystals have few practical applications they serve as very hospitable host crystals for the study of electronic structures of transition metal ions. Mention was made earlier in this article of the magnetic properties of RbMnF_3 , which has the same cubic structure as KMgF_3 . These

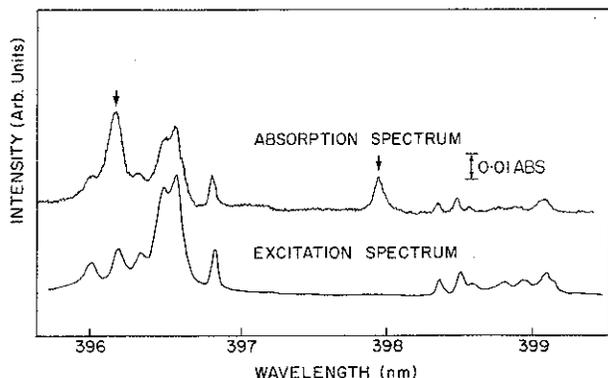


Fig 10 Ground-state absorption spectrum (top) and luminescence excitation spectrum (bottom) of a single KMgF_3 crystal containing Mn at 15°K. The absorption due to manganese-nickel pairs is shown by the arrows.

magnetic properties arise as a result of the interaction between nearest neighbor manganese ions sharing an intervening fluoride ion. Full comprehension of interactions requires a prior understanding of the electronic structure of the single manganese ion, which depends on a detailed knowledge of its absorption spectrum. This spectrum can be measured using crystals of KMgF_3 doped with small amounts of manganese (about one manganese atom for 99 magnesium atoms). The manganese impurity replaces the magnesium simply, and the octahedron of six fluoride ions around it produces an arrangement which is the simplest one for theoretical analysis. However, there are complications. First, the very weak absorption of such a manganese ion makes the direct measurement of its absorption spectrum difficult unless very large crystals are available. Second, if a MnF_6^{4-} octahedron has a similar octahedron as one of its six neighbors then the absorption spectrum is different (in wavelength and intensity) from that of one MnF_6^{4-} having six MgF_6^{4-} neighboring octahedra. We refer to the pair as an exchange-coupled pair of Mn^{2+} ions, and a study of its absorption spectrum provides information about the magnetic coupling between Mn^{2+} ions. Third, if Ni^{2+} is a trace impurity in any of the starting materials, then we have to contend with the absorption by the NiF_6^{4-} octahedron plus the pair comprising MnF_6^{4-} and NiF_6^{4-} (an exchange-coupled pair of Mn^{2+} and Ni^{2+} ions).

As Mn^{2+} in KMgF_3 luminesces in the orange-red region of the spectrum while Ni^{2+} in KMgF_3 luminesces in the near infrared and weakly in the green region, a photomultiplier detector (insensitive to infrared radiation) and a red filter eliminate the luminescence of Ni^{2+} and detect only that from the Mn^{2+} . Therefore, by recording the amplified photomultiplier response to the orange-red luminescence as we scan the 1402 spectrometer through the wavelengths from about 600 nm to about 220 nm, we obtain a spectrum of exciting wavelengths which bear a direct relationship to the absorption spectrum of the Mn^{2+} . To illustrate the power of this technique, the measured absorption spectrum [9] and the excitation spectrum of a KMgF_3 crystal containing Mn^{2+} are shown in Fig 10. The absorption by the exchange-coupled Mn^{2+} pairs is shown by the arrows. One further point to note is that the two spectra shown in Fig 10 were recorded simultaneously, so that sample conditions are exactly the same in both.

Excited State Absorption Spectra

As mentioned previously, there is a dark phase during each cycle of the chopper wheels. During this time the sample can be irradiated by a pulsed laser (triggered by the gating circuit of the double beam attachment) to create a metastable excited state of the crystal. The time for one complete cycle of each chopper wheel is about 37 msec so that, if the lifetime of the metastable state is at least this long, the absorption spectrum of the metastable state can be measured.

For this technique it is essential to have the laser exciting light and the double beam probe light traverse the same region of the sample. It is, of course, also necessary to have the highest possible power density of exciting light to maximize the concentration of metastable species. Small crystals and the microscope optics optimize these two conditions with the arrangement shown in Fig 11. For our work we have selected a tunable dye laser (Moletron DL 200), focusing the beam (via the 45° mirror in Fig 11) by a lens attached to the side of the sample compartment of the double beam attachment.

One limitation of this technique is luminescence from the metastable state when it lies in a spectral range to which the photomultiplier tube is sensitive. The technique is ideal for measuring the triplet-triplet absorption spectra of organic molecules in crystals.

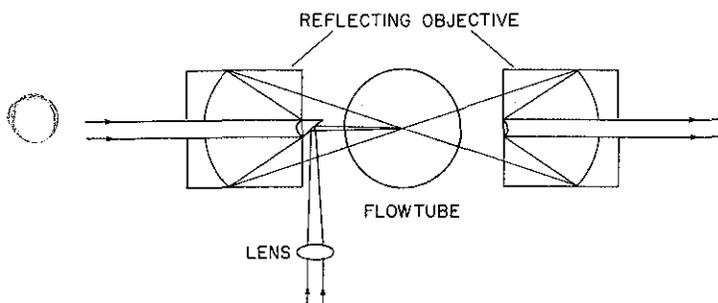


Fig 11 Optical arrangement for the measurement of excited state absorption of small single crystals under laser excitation.

Luminescence Emission Spectra

In order to measure luminescence emission spectra we take advantage of the symmetrical optical arrangement of the 1402 spectrometer and place a photomultiplier at the normal entrance slit. To make this change quickly we place a 45° swingaway mirror on the entrance slit to reflect the luminescence light to the photomultiplier. The tunable dye laser excites the luminescence with the same arrangement shown in Fig 11.

The particularly powerful feature of this system is the dye laser with its tunable, narrow line width. This enables us to selectively excite luminescence from different species or from the same species in different crystal sites, opening up the possibility of a large number of different studies, including those of contaminant molecules in molecular crystals, of ions and ion pairs in ionic crystals, and of the same species in inequivalent crystal sites.

Photochemical Studies

Part of our research program involves the photodimerization of molecules in crystals [10, 11]. In particular we are studying anthracene and a number of its derivatives. The photodimerization of anthracene molecules to form dianthracene has been known for about 70 years, but it is only in recent years that progress has been made in explaining the mechanism of this reaction which underlies an important branch of photochemistry.

Photochemistry is a growing innovative area, and the availability of solar energy as a radiation source is an obvious reason for increased interest in this field. Reversible photodimerizations have some potentially practical applications because the dissociation of the photodimer is usually an exothermic reaction, which means heat is given out. Solar energy can promote the photodimerization, and a part of the energy can be recovered in a subsequent thermal dissociation of the photodimer. Obviously, an understanding of such a reaction is essential to the successful development of theoretical models of photochemical behavior.

Our approach has been to start with a single crystal of a dianthracene-related compound. If this crystal is irradiated with light of wavelength less than about 300 nm the molecules of the crystal are photolysed — carbon-carbon bonds connecting the two halves of the photodimer are broken, and the constituent pair of molecules is released (two anthracene molecules in the case of dianthracene). Because these two molecules occupy the space previously occupied by the photodimer, and there are other photodimer molecules adjacent to them, they are unable to move apart. If light of longer wavelength, absorbed by the pair of molecules, now irradiates the crystal, photodimerization of the molecules is achieved. Both of the irradiations can be carried out with the sample in the flow tube, for any selected temperature, simply by opening the slits of the 1402 to 2-3 mm. After a suitable time has elapsed the slits are reduced in width, and the absorption spectrum of the molecule pairs is determined. The rate of photodimerization can be determined by monitoring the absorption spectrum. Sometimes the rate of photodimerization is dependent on the crystal temperature, and low temperatures inhibit the photodimerization so that luminescence can be observed. In these cases the luminescence spectrum can be measured as outlined above.

The most important feature of the present experimental arrangement is that a variety of spectroscopic measurements can be carried out at a variety of controllable sample temperatures without the need to move the sample or to change its temperature.

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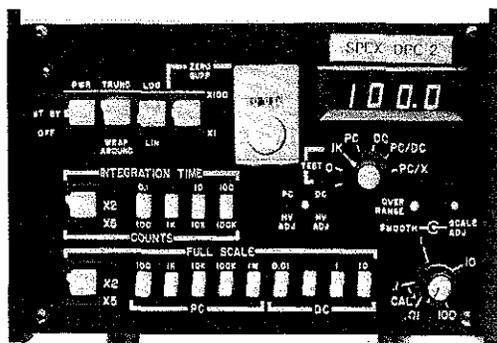
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