Spectroscopy of Ionic Crystals:
The Hydrogenated Calcium Fluoride System*

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Abstract

This paper reviews the spectroscopy of ionic crystals, taking the system of hydrogenated calcium fluoride crystals containing trivalent rare earth ions as a specific example to illustrate the kinds of information that can be obtained by spectroscopic means. The discussion is primarily directed to solid state physicists who are not specialists in spectroscopy.

Introduction

The spectroscopy of solids is a branch of physics concerned with the interaction of electromagnetic radiation with solids. In the spectra one can observe vibrational features due to the nuclear motion of the constituent ions and electronic effects due to excitation of electrons between energy levels of the solid. For metals and semiconductors and for excitons it is appropriate to use band theory for the description of their electronic behaviour, while for ionic crystals an atomic wavefunction treatment is more appropriate. The purpose of this paper is to review the spectroscopy of ionic crystals with the emphasis on the physics information that can be obtained using spectroscopic methods.

The spectroscopy of ionic crystals uses several techniques, including the following.

(i) *Absorption*

Light whose photon energy $h\nu$ matches the energy difference $E_f - E_i$ between an excited state of energy E_f and a ground state of energy E_i satisfies a condition for absorption to occur. The frequency plot of light intensity transmitted by the material comprises its absorption spectrum. This gives a direct measure of the energies of the various quantum levels of the material.

Allowance needs to be made for reflectivity losses, which occur when light is incident on a transparent medium of refractive index n, before the true absorption can be determined. For a parallel sided slab of material of index n the transmission T of light at normal incidence is defined by

$$T = 2n/(n^2 + 1)$$

and is independent of the thickness. The reflectivity correction is usually negligible for ionic crystals in their region of transparency.

(ii) *Fluorescence*

Irradiation of a material can result in emission of light at longer wavelengths. These transitions occur through processes in which the material absorbs a photon and emits another from a lower energy state possessing a finite lifetime for emission.

Fluorescence spectra are frequently richer in lines than absorption spectra as there can be transitions between many pairs of levels whereas absorption spectra are limited to transitions originating from the ground state or from levels within a few kT of it.

(iii) *Excitation*

If, in a fluorescence emission experiment, the frequency of the exciting light is in a spectral range where the material is purely transparent, the fluorescence emission is zero. If, on the other hand, the excitation frequency is in a spectral region where some absorption is present the fluorescence can be appreciable even if the absorption is very weak. Monitoring of the fluorescence spectrum of a material as the frequency of the exciting light is varied can therefore reveal the presence of absorption bands too weak to be observed without studying inordinately thick samples.

(iv) *Time resolution*

Fluorescence transitions occur from energy states possessing a finite lifetime for emission. If the incident light is pulsed or chopped, one can measure the intensity of emission as a function of time. If several emitting species of different lifetimes are present, their emissions are usually resolved by their different frequencies using a spectrometer. One can resolve the emissions further by, for example, altering the time of observation after the excitation pulse. Such time resolution techniques can correlate different transitions arising from a common upper emitting level.

(v) *Scattering*

Scattering is a process in which incident light is altered in spatial direction by a material. The scattering may be elastic (Rayleigh scattering), where no frequency change in the light occurs, or inelastic. The inelastic scattering process, in which the frequency of the light is altered (Raman scattering), is useful for spectroscopic studies since the observed frequency shifts correspond to the energies of various excitations of the crystal, such as phonons, excitons and magnons. The scattering occurs through two-photon processes in which one photon is absorbed (or emitted) and another emitted (or absorbed), and is a weak effect. Raman scattering therefore requires intense laser sources for adequate intensity Raman lines and double monochromators for the elimination of incident radiation from the spectra.

Raman scattering measurements are similar to fluorescence measurements in many experimental aspects. However, Raman scattering and fluorescence occur by quite different processes. Raman lines can be distinguished experimentally from fluorescence lines since Raman lines have a constant frequency shift from the incident light frequency whereas fluorescence lines have an absolute frequency independent of the incident light frequency. Time resolution studies can also be used to resolve Raman lines from fluorescence lines on the basis of the finite lifetimes associated with fluorescence processes.

Rather than give further details here of the above techniques, their use and application will be illustrated by considering the specific example of calcium fluoride crystals, both with and without hydride ions and trivalent rare earth ions as impurities. This

system displays many of the interesting aspects of the spectroscopy of ionic crystals and is a good example to give an idea of what kind of information can be obtained by using spectroscopic techniques. It has been studied extensively over many years by researchers at the University of Canterbury, New Zealand, Hebrew University of Jerusalem, Israel, University of Reading, England, and the University of Groningen, Netherlands, among others (e.g. Newman 1973; Timans and den Hartog 1976; Koster and den Hartog 1977).

The study of ions introduced as impurities in ionic crystals has a two-fold purpose. Firstly, the electronic energy level scheme of the ion itself is frequently of interest. For this purpose the host crystal provides a well-defined environment for the impurity ion and is chosen to be transparent over the region of interest. The energy levels of the impurity ion can be measured down to low temperature, in contrast to the situation in atomic spectroscopy, and the effect of external perturbations such as stress or magnetic fields, can also be studied. Secondly, an impurity ion can be used as a probe to deduce a variety of information about the host crystal. This aspect is also frequently used in e.p.r. and Mössbauer spectroscopies where ions, such as [57]Fe for Mössbauer, yield information about their host crystals such as electric quadrupole fields, internal magnetic fields etc., which may not be readily obtainable otherwise.
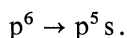
Ionic Crystals

In an ionic crystal the ions carry opposite charges and in the infrared active transverse optical mode of vibration, a dipole moment is generated. Because this moment interacts strongly with electromagnetic radiation all ionic crystals have a very intense absorption called reststrahlen absorption (Brown 1967). The name 'reststrahlen' comes from the fact that the crystals also strongly reflect in the same spectral region. For calcium fluoride this absorption peaks at 257 cm^{-1} and crystal thicknesses of less than 10 μm are necessary to obtain appreciable light transmission at the peak absorption. Homopolar crystals, such as silicon or germanium, do not show intense infrared absorption of this type and the phenomenon is characteristic of ionic crystals.

The affect of defects on the vibrations of ionic crystals is to perturb all the frequencies and, in some cases, new frequencies of vibration are produced. When a very light ion is substituted for a regular ion in a diatomic crystal, one of the frequencies emerges from the top of the optical band of lattice frequencies and forms a discrete localized mode well above the highest frequency of the host lattice. This is well localized about the light ion and decays exponentially away from it. If the light ion is charged, the frequency of the localized mode can be determined by infrared absorption spectroscopy.

For very heavy ions substituting for regular ions no discrete modes are expected, but resonance modes about the heavy ion are produced. These modes may be detected by far infrared spectroscopy in the region below that of the intense reststrahlen absorption of the host crystal.

Ionic crystals are transparent through the visible and near ultraviolet, but absorb strongly in the ultraviolet above about 7 eV (56000 cm^{-1}). The absorption is very strong and the onset occurs in calcium fluoride at $10 \cdot 3$ eV (83000 cm^{-1}). The spectra are all similar for a given halide and the transitions are charge transfer, and may be interpreted approximately as the excitation of the p^6 halide shell:

$$p^6 \rightarrow p^5 s.$$

Calcium fluoride crystals are transparent in millimetre thicknesses from $750\ \text{cm}^{-1}$ in the infrared to $80\,000\ \text{cm}^{-1}$ in the ultraviolet. The crystals have a body-centred cubic structure; each calcium ion is surrounded by eight fluorine ions at the corners of a cube and every second cube of fluorine is empty (Fig. 1).
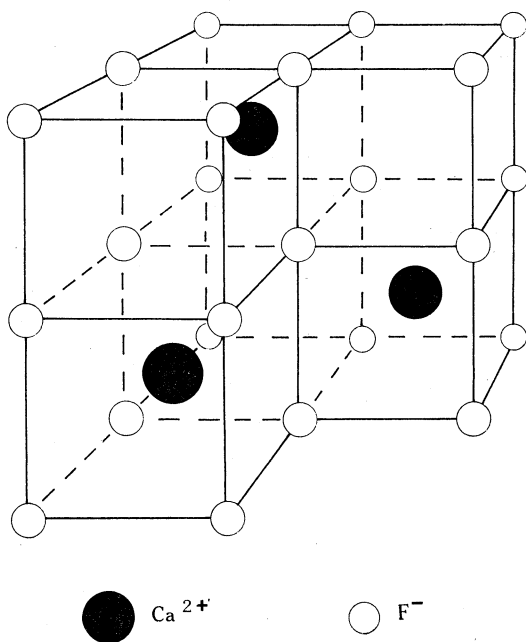
Fig. 1. Calcium fluoride lattice.

Ca $^{2+}$ F $^{-}$

Local Modes of Hydrogen in Calcium Fluoride

Hall and Schumacher (1962) showed that hydrogen and deuterium will dissolve readily in calcium fluoride if the crystals are heated in the gas at $800°C$ in the presence of aluminium. The crystals then show sharp lines in the infrared which are assigned as localized vibrations of H^- and D^- ions in the fluorine sites (Elliott *et al.* 1965).

In the alkali halides the defect of a H^- ion substituting for the anion is known as the U centre and gives rise to a strong optical absorption band in the ultraviolet region which corresponds to an electronic transition in the centre, and to an absorption in the infrared region which is associated with the vibrational motion of the defect. The lines observed here for calcium fluoride are the analogues of those of the U centre in the alkali halides.

The primary observation is the frequency of the localized mode and from this one can deduce information about the localization of the mode and the interatomic force constants in the vicinity of the impurity ion. The local mode for H^- in calcium fluoride has a frequency of $965\ \text{cm}^{-1}$, which is well above the highest frequency ($463\ \text{cm}^{-1}$) of the lattice vibrations of calcium fluoride. The local mode is therefore strongly localized about the H^- ion and, to a good approximation, the rest of the lattice may be taken as static. The same approximation is less satisfactory for D^- where the localized mode will extend a little, and this is reflected in the relative frequencies of H^- and D^-. For D^- in calcium fluoride the local mode has a

frequency of 694 cm^{-1} and $\omega_H^2/\omega_D^2 = 1.92$ while for independent oscillation of the particles it would be 2, the inverse mass ratio.

The hydride ion thus moves in a potential well which may be expanded in a power series in its displacement (X, Y, Z) from equilibrium. For a hydrogen ion in the fluorine ion site, the potential V has the form

$$V = V_0 + A(X^2 + Y^2 + Z^2) + BXYZ + C_1(X^4 + Y^4 + Z^4)$$
$$+ C_2(X^2Y^2 + Y^2Z^2 + Z^2X^2), \tag{1}$$

while, for the cubic symmetry Ca^{2+} and interstitial sites, the constant B is zero. In the harmonic approximation, the angular frequency of the localized mode is $(2A/m)^{\frac{1}{2}}$, where m is the light ion mass. The frequency of the H^- local mode is somewhat lower than would be expected for a change of anion mass only in calcium fluoride, and Elliott et $al.$ (1965) concluded that the force constants A binding the H^- are weaker than those binding F^-.

Anharmonic effects in the crystal (represented by the B and C terms in the potential V of equation 1) allow us to see harmonics of the main transitions and structure in the main line and also to account for the linewidths observed. For H^- in calcium fluoride there is one second harmonic of the 965 cm^{-1} mode at 1919 cm^{-1} and two third harmonic lines at 2912 and 2826 cm^{-1}. An estimate of the degree of anharmonicity can be deduced from the frequency shift of the second harmonic line away from twice the fundamental frequency. From such shifts Elliott et $al.$ (1965) obtained the anharmonic constants B, C_1 and C_2 for the potential well in which the H^- ion is vibrating.

The occurrence of a second harmonic line is conclusive evidence that the hydrogen and deuterium ions are in the fluorine sites. Selection rules do not allow a second harmonic for H^- or D^- ions in the cubic symmetry Ca^{2+} or empty interstitial sites. Other harmonic lines not allowed for infrared absorption have been detected by Hayes and Macdonald (1967) using uniaxial stress to relax the selection rules, and by Harrington et $al.$ (1970) using Raman scattering.

The linewidth of the main local mode line changes from 8.7 cm^{-1} at 300 K to less than 0.7 cm^{-1} at 20 K for H^- in calcium fluoride and from 6.5 cm^{-1} at 300 K to 2.2 cm^{-1} at 20 K for D^- in calcium fluoride. The low temperature width is due to spontaneous decay of the local mode excitation into lattice modes. This is greater for D^- than for H^- since the former can arise from decay into two lattice modes while the latter requires at least three lattice modes (965 > 2 × 463 cm^{-1}). However, the temperature-dependent width is greater for hydrogen because of its larger amplitude of vibration.

Rare Earth Ions in Crystals

The rare earths are characterized by the progressive filling of the 4f shell. Because of the so-called lanthanide contraction, the f shell behaves as an inner shell relatively well shielded from the environment. In solids the rare earths usually occur as trivalent ions. Their low temperature spectra consist of groups of sharp lines whose positions vary only slightly for different host crystals and may be correlated with the positions of the energy levels of the 4f^n configuration of the free trivalent ions (Wybourne 1965; Dieke 1968). Each group of lines corresponds to an LSJ multiplet and is $(2J+1)$-fold degenerate.

When the ion is placed in a crystal, each multiplet is split into several crystal field levels by the environment. The number and degeneracy of the levels depend on the point symmetry about the rare earth ion. Lea *et al.* (1962) have given the results for the case of rare earth ions in cubic symmetry.

In calcium fluoride the trivalent rare earth ions substitute for the divalent calcium ions and require charge compensation for overall charge neutrality. There are many ways in which charge compensation may be achieved and this is reflected in the complexity of the optical and e.p.r. spectra. Each site yields its characteristic spectrum and all these appear superposed in the overall spectrum. Weber and Bierig (1964) and Baker (1974) give summaries of the various charge-compensation mechanisms determined by e.p.r. while numerous studies have been made of the optical spectra.
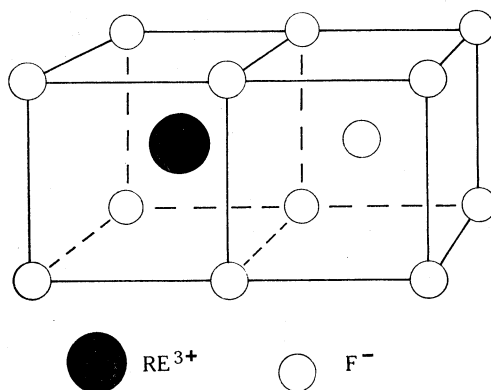

Fig. 2 Tetragonal symmetry sites of the trivalent rare earth ion and the interstitial fluoride ion.

Some of the trivalent rare earth ions are found to have cubic symmetry characteristic of the substituted Ca^{2+} ion. In these cases the charge compensation is not achieved locally. A common form of charge compensation is provided by an interstitial fluoride ion in an empty fluorine cell adjacent to the trivalent rare earth ion. Both the F^- ion and the trivalent rare earth ion have tetragonal symmetry (Fig. 2). This arrangement is the best characterized of the many arrangements possible in CaF_2. Other arrangements involving single or multiple fluoride ions at more distant interstitial sites and others involving oxygen charge compensation can be readily visualized.

There are several methods for distinguishing the spectra of trivalent rare earth ions in each charge-compensation arrangement. One of these is the concentration series method in which the spectra of a series of crystals of varying rare earth concentration are compared to determine which lines correlate in intensity and to which e.p.r. spectra they are related. An example of this method is the work done on neodymium spectra by Voron'ko *et al.* (1966).

A second method for distinguishing spectra is that of rotational Zeeman studies of the optical lines, in which the crystal is rotated about a symmetry axis in a magnetic field and the variation of the magnetic field splitting of the lines is followed. This method gives the symmetry of the charge-compensation sites directly, and it has been done for erbium by Rector *et al.* (1966).

A third method is to use time resolution techniques. The lifetimes of fluorescence lines of the various charge-compensation arrangements can differ appreciably. For example, for $CaF_2 : Gd^{3+}$, the usual F^- charge compensation site has a lifetime of 11 ms at 77 K, the hydride ion analogue (to be discussed below) has 4 ms, the deuterium ion analogue has 3 ms, while the oxygen charge-compensation site has $1 \cdot 5$ ms. Use of a rotating chopper to successively irradiate and observe the crystals enables the lines of these different charge-compensation sites to be separated (e.g. Peled *et al.* 1966). With the advent of mode-locked lasers, this technique can be expected to become more widely used, particularly for rare earth ions whose lifetimes are in the low microsecond range.

A further method is that of selective laser excitation, where each charge-compensation site is separately excited by radiation from a suitably tuned dye laser. This method has been used by Kliava *et al.* (1978) for analysing praseodymium spectra and by Tallant and Wright (1975) for erbium spectra. It has also been used successfully by C. A. Freeth (personal communication) to select just those tetragonal symmetry charge-compensation arrangements whose rare-earth–fluoride ion axes lie transverse to an applied magnetic field.

Hydrogen Local Modes in Calcium Fluoride Crystals containing Rare Earth Ions

In hydrogenated crystals of calcium fluoride containing trivalent rare earth ions, interstitial hydride ions may also be involved in charge compensation, and it is found that some of the rare earth ions have hydride ions at a nearest neighbour interstitial ion site and form rare-earth–hydride ion pairs exactly analogous to the rare-earth–fluoride ion pairs of tetragonal symmetry described above.

In the infrared, the crystals show two additional local mode lines due to these hydride ions. Their frequencies vary with the particular rare earth ion present, the separation of the two lines being largest for lanthanum at the beginning of the rare earth series and decreasing monotonically towards the lutecium end of the series. This variation in separation follows the decrease in the radii of the rare earth ions with increasing atomic number (Jones *et al.* 1969). The low frequency line is assigned as the doubly degenerate 'transverse' hydride ion vibration and the high frequency line as the 'longitudinal' vibration. The low frequency line in calcium fluoride containing cerium is verified to be the doubly degenerate one since it splits into two components that are observable under high resolution, due to electron–phonon interaction effects (Jacobs *et al.* 1971).

Harmonics of the local mode lines can be observed in crystals of several centimetres thickness. Their number is fully consistent with the assignment of the local mode lines to the tetragonal symmetry rare-earth–hydride ion pairs.

Strontium fluoride shows analogous local mode lines to those of calcium fluoride for the rare earth ions in the earlier part of the series. However, for the heavier rare earth ions beyond terbium the local mode spectra radically change due to the preferential occurrence of other charge-compensation arrangements (Edgar *et al.* 1977).

Electron–Phonon Interaction Effects

The coupling between the electronic states of the rare earth ion and the local mode of the hydride ion manifests itself (i) as a shift in the electronic levels of the rare earth ion in the changed environment due to the hydride ion, (ii) as an isotope shift

for these levels when deuteride ions are substituted for hydride ions, and (iii) in the occurrence of vibronic transitions involving the hydride ion local modes.

(i) *Shift in electronic levels*

After hydrogenation the rare earth ion spectra show additional lines at slightly longer wavelengths than the usual electronic transitions and these are transitions between electronic states of the rare earth ions situated in a site where there is a hydride charge-compensation ion present. The substitution of a hydride ion for a fluoride ion in a given charge-compensation arrangement can affect the energy levels in two ways: (1) through an altered crystal field acting on the rare earth ion, and (2) through a change in the covalent bonding of the rare earth ion to its neighbours, arising from the different ionic radius and electronegativity of a hydride ion as compared with a fluoride ion. Both effects can be quantitatively determined. The crystal field change can be summarized as follows. For the larger radius rare earth ions near the beginning of the rare earth series, the hydride ion provides an axial crystal field about twice that provided by a fluoride charge-compensating ion, while the cubic field provided by the eight nearest neighbour cube of fluoride ions is reduced by about 30%. As one goes along the rare earth series to those whose ionic radii are less than that of calcium, the crystal field provided by the hydride ion approaches that of the fluoride charge-compensation ion. By erbium, the axial crystal field due to the hydride ion is only 11% larger than that due to an interstitial fluoride ion. All these results can be qualitatively visualized on the model of a larger or smaller rare earth ion replacing a divalent calcium ion and altering the position of the four fluoride ions between it and its charge-compensating ion to a greater or lesser extent. The charge-compensating ion, itself, is also displaced towards the rare earth ion by an amount depending on the radius of the latter (Kiro and Low 1969, 1970).

The covalency effect, which causes a shift in the centre of gravity of each multiplet, is only a relatively small effect and the change in going from fluoride ion to hydride ion charge compensation is only a decrease of about 0·2%. The smallness of the effect is partially due to the fact that only one next nearest neighbour charge-compensating ion, outside the eight fluoride ions surrounding the rare earth ion, is substituted.

(ii) *Isotope shifts*

Corresponding deuterated crystals also show electronic lines whose frequencies are slightly different from those produced by hydrogenation. Crystals heated in a 1 : 1 hydrogen–deuterium atmosphere display both lines.

The crystal field acting on the rare earth ion is modulated by the hydride or deuteride ion vibrational motion, and the change in the amplitude factor $(\hbar/2m\omega)^{\frac{1}{2}}$ between hydrogen and deuterium results in a shift of the D^- charge-compensated rare earth ion lines relative to those of a H^- charge-compensated rare earth ion. The shift can turn out to be positive or negative. An order of magnitude estimate of the isotope shift can be obtained as follows.

The mean square displacement of the hydride ion is, for a 1000 cm^{-1} vibration,

$$\langle \Delta x \rangle^2 = \hbar/2m\omega = 1\cdot74 \times 10^{-22} \quad \text{m}^2.$$

The separation R of the trivalent rare earth ion from the hydride ion is $2\cdot73$ Å, giving $\langle \Delta x \rangle^2/R^2 \approx 2 \times 10^{-3}$. A conservative and reasonable estimate of the crystal field

due to a single hydride ion acting on a trivalent rare earth ion that is distance R away is 500 cm^{-1}. Hence the isotope shift is of the order of

$$(2 \times 10^{-3})\,(500)\,(1 - 1/\sqrt{2}) = 0 \cdot 3 \quad \text{cm}^{-1},$$

which is in qualitative agreement with the shifts found experimentally.

(iii) *Occurrence of vibronic transitions*

Since the local mode frequencies of both hydrogen and deuterium are considerably higher than the lattice frequencies of calcium fluoride, vibronics occur well above the much stronger vibronic spectrum of the pure crystals. The frequency separations of these vibronics from their parent electronic lines match the frequencies of the localized mode lines observed in the infrared, which confirms the assignment of the rare earth ion optical lines to a particular hydride ion charge-compensation arrangement. However, a small discrepancy occurs between the local mode frequencies deduced from the vibronic spectra and those observed directly in the infrared, and these differences are the local mode vibronic shifts. They originate from the same electron–phonon interaction responsible for the isotope shifts of the rare earth electronic lines.

A clear-cut manifestation of the local mode vibronic shift is the observation of the anomalous four-line local mode spectrum of erbium (Jones *et al.* 1969). Chambers and Newman (1969) correctly surmised that the four lines are two pairs: one associated with the ground state of the erbium ion and the other with a low-lying crystal field level of erbium. Edgar *et al.* (1979) determined from optical studies that this low-lying level was $4 \cdot 5$ cm^{-1} above the ground level for the hydrogenic site, $2 \cdot 7$ cm^{-1} for the deuterium site and $2 \cdot 2$ cm^{-1} for the tritium site, and hence is appreciably populated down to 4 K. In the absence of any electron–phonon interaction effects there would be two coincident pairs of lines in the local mode spectrum, but the different electron–phonon interaction shifts for the two crystal field levels result in non-coincidence and four distinct lines in the spectrum.

Another manifestation of electron–phonon interaction effects is the vibronic splitting of the doubly degenerate 'transverse' local mode line referred to above. For rare earth ions with degenerate electronic ground states, the coupling between this local mode line and excited rare earth ion electronic levels of similar energies, i.e. approximately 1000 cm^{-1}, can raise the degeneracy of this 'vibronic' to give structure. Such results have been demonstrated for cerium by Jacobs *et al.* (1971) and for praseodymium by Jacobs (1971).

Electron–phonon interaction effects are expected to be considerably enhanced for transitions involving 5d states, because these are not shielded like the 4f states. The cerium ion system is convenient for these studies because of the occurrence of 4f→5d electronic transitions near 30 000 cm^{-1}, i.e. in a spectral region readily accessible to experimental study. Relatively large effects were found by Jacobs *et al.* (1971) for these transitions in hydrogenated crystals of calcium fluoride containing cerium.

Reorientation of Trivalent Rare Earth Charge-compensating Ion Dipoles

In conclusion, some mention should be made of spectroscopic and electrical measurements concerning reorientation of the trivalent rare earth ion – fluoride ion and trivalent rare earth ion – hydride ion pairs in calcium fluoride. The charge-com-

pensating ion can migrate between several equivalent positions and this thermally activated hopping motion is equivalent to the reorientation of the electric dipole formed by the trivalent rare earth ion and its charge compensator. This manifests itself in several ways: (1) as a lifetime broadening of the rare earth ion e.p.r. lines, (2) as a contribution to the dielectric loss of the crystal, and (3) as a contribution to the ionic thermal current when the dipoles, partially oriented by applying an electric field to the crystal at low temperature, relax back to their equilibrium distribution on warming the crystal in the absence of the field. Franklin and Marzullo (1970) have measured the relaxation times of the trivalent gadolinium–fluoride ion dipoles by both the e.p.r. broadening technique and dielectric loss measurements. Edgar and Welsh (1975) have reported similar measurements on the corresponding hydrogen and deuterium dipoles. Stott and Crawford (1971a, 1971b), Kitts (1973), Kitts et $al.$ (1973) and Kitts and Crawford (1974) have applied the ionic thermal current (ITC) technique to the study of the same dipolar species. Overall, the fluoride dipoles give clear-cut results while only indirect evidence of reorientation is obtained for the hydride dipoles, due to the inability to produce crystals containing more hydride than fluoride ion dipoles.

Acknowledgments

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