OPTICAL ABSORPTION SPECTRA OF H_2O ICE DOPED WITH YTTERBIUM CHLORIDE $YbCl_3$

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ABSTRACT. Near-infrared absorption spectra of a frozen dilute solution of ytterbium chloride have been obtained at 77 K, 20 K, and 4.2 K. They contain two broad lines revealing a Stark splitting of 60 cm^{-1} of the excited $^2F_{5/2}$ level of the Yb^{3+} ion. Such spectra indicate that in frozen solutions of ytterbium chloride the Yb^{3+} ions have crystalline or quasi-crystalline surroundings which are similar for most ions; different possibilities are discussed.

RÉSUMÉ. *Spectres d'absorption optiques de la glace H_2O dopée avec du chlorure d'ytterbium $YbCl_3$.* Les spectres d'absorption dans l'infrarouge proche d'une solution diluée gelée de chlorure d'ytterbium ont été obtenus à 77 K, 20 K et 4.2 K. Ils présentent deux larges raies dont la séparation (60 cm^{-1}) correspond à une décomposition par effet Stark du niveau excité $^2F_{5/2}$ de l'ion Yb^{3+}. Ces spectres montrent que, dans les solutions gelées de chlorure d'ytterbium, la plupart des ions Yb^{3+} ont un entourage cristallin ou quasi-cristallin semblable; differentes possibilités sont discutées.

ZUSAMMENFASSUNG. *Optische Absorptionsspektren von H_2O-Eis, dotiert mit $YbCl_3$-Ytterbiumchlorid.* Die Absorptionsspektren im nahen Ultrarot einer gefrorenen verdünnten Lösung von Ytterbiumchlorid wurden bei 77 K, 20 K und 4.2 K aufgenommen. Sie zeigen zwei breite Linien, deren Abstand (60 cm^{-1}) von einer Stark-Effekt-Aufspaltung des angeregten Niveaus $^2F_{5/2}$ des Yb^{3+}-Ions herrührt. Derartige Spektren zeigen, dass in gefrorenen Lösungen von Ytterbiumchlorid, die meisten Yb^{3+}-Ionen eine gleichartige kristalline oder quasi-kristalline Umgebung haben; verschiedene Möglichkeiten werden diskutiert.

INTRODUCTION

Earlier work (Couture and Le Paillier-Malécot, 1975; Couture, 1977) has shown that some frozen dilute solutions of rare-earth salts exhibit optical absorption line spectra which reveal a splitting of the electronic energy levels of the rare-earth ions such as appears when such ions are located in a crystalline field.

High-pressure experiments at low temperatures (Jean-Louis and Couture, in press) have shown that this phenomenon appears only under conditions of temperature and pressure where the hexagonal Ih ice phase should be present (and not where phases II, III, IX, and Ic should appear).

We present here the results obtained from near-infrared absorption spectra of a frozen aqueous solution of ytterbium chloride $YbCl_3$ at atmospheric pressure and low temperatures. This study may shed light on the reason why the attempt to use frozen ytterbium chloride solutions as a substance for a proton-spin refrigerator was unsuccessful (Lichti and Stapleton, 1973).

EXPERIMENTAL TECHNIQUES

The ytterbium chloride solution was prepared by dissolving 86.29 mg of Yb_2O_3 in 10 cm^3 of an aqueous solution of 1.2N hydrochloric acid; the result was an aqueous solution whose molarity in $YbCl_3$ was 0.044 mol l^{-1}. The frozen solution was obtained by lowering the temperature at a rate of the order of 1 K min^{-1}. The cell containing the frozen sample was then immersed in liquid nitrogen, hydrogen, or helium at temperatures of 77 K, 20 K, or 4.2 K. The experimental arrangement for absorption spectroscopy has been described by Couture and Le Paillier-Malécot (1975). The spectra have been recorded on Kodak IQ near-infrared-sensitive photographic plates.

EXPERIMENTAL RESULTS

The absorption spectra of frozen dilute solutions of ytterbium chloride exhibit only two broad lines (Fig. 1). Table I gives the wave numbers σ, the line widths w, and the relative intensities I, of the lines at temperatures of 77 K, 20 K, and 4.2 K. The wave numbers are measured with an estimated error of ± 5 cm^{-1} (1 cm^{-1} corresponds to a frequency of 30 GHz). Between 77 K and 4.2 K the spectra change very little with temperature.

Frozen dilute solution of ytterbium bromide YbBr$_3$, ytterbium bromate Yb(BrO$_3$)$_3$, or ytterbium nitrate Yb(NO$_3$)$_3$ at 77 K exhibit, in the same spectral region, only a very broad band whose width is about 300 cm^{-1}, similar to the band presented by aqueous liquid solutions of ytterbium salts (Hoogschagen, 1946; Carnall and others, 1968).
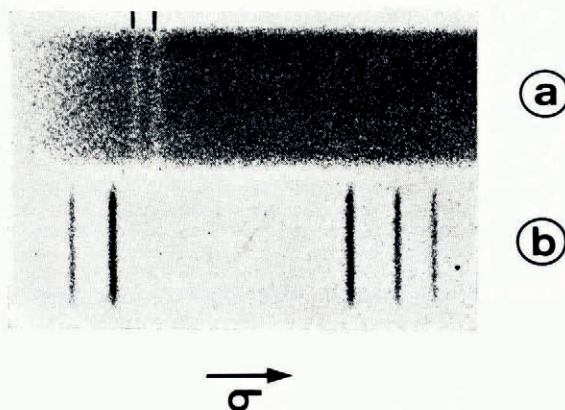

Fig. 1. (a) Absorption spectrum of frozen YbCl$_3$ aqueous solution at $T = 20$ K, and (b) reference xenon emission spectrum.

TABLE I. PARAMETERS OF ABSORPTION LINES

$T = 77$ K			$T = 20$ K			$T = 4.2$ K		
σ cm^{-1}	w cm^{-1}	I	σ cm^{-1}	w cm^{-1}	I	σ cm^{-1}	w cm^{-1}	I
10 275	45	8	10 267	40	6	10 272	40	6
10 330	50	10	10 329	50	10	10 331	50	10

DISCUSSION

The ytterbium ion Yb^{3+} has a configuration 4f^{13}; as one electron is lacking to fill the shell there is only one term ^{2}F which gives two levels ^{2}F$_{7/2}$ and ^{2}F$_{5/2}$ by L–S coupling. For the free ion these two levels have degeneracies respectively of 8 and 6 and they are 10 214 cm^{-1} apart (Kaufman and Sugar, 1976). When ytterbium ions occupy definite sites in crystals each level is split into Stark components by the crystalline electric field and optical transitions may occur between those Stark levels. Figure 2 shows a possible schematic level diagram of the ytterbium ion Yb^{3+} in free space, in a cubic field, and in a field of lower symmetry (the degeneracies of the levels are indicated in parentheses).

The fact that in the absorption spectra that we have obtained there is no line of which the intensity varies with temperature in the range 4 K–77 K indicates from Boltzmann's law that there is no level in the vicinity of the lowest sub-level, at least in a region of 50 cm^{-1}. As a consequence we conclude that the two lines arise from transitions starting from the lowest

sub-level. The separation of the two lines must then be interpreted as a Stark splitting of the excited level. The magnitude of that splitting (≈ 60 cm^{-1}) is of the same order as the splittings occurring for rare-earth ions located in crystalline matrices.

The fact that only two lines are observed could be explained by a cubic or nearly cubic symmetry (cf. Fig. 2). But, as Dieke and Crosswhite (1956) have pointed out, such two-line spectra may also occur in a field of hexagonal symmetry; they thus explained the appearance of only two strong lines (at 10 282 and 10 297 cm^{-1}) in the spectrum of an Yb doped YCl$_3 \cdot 6$H$_2$O crystal for which the Zeeman effect had an approximately axial symmetry.

The width of the lines (Table I) varies very little with temperature and remains large even at 4.2 K. It is interesting to note that this width (≈ 50 cm^{-1}) is characteristic of the spectra of frozen solutions, as it is about ten to one hundred times larger than the width of lines of rare-earth ions in crystals at low temperature and about ten times less than for liquid solutions.

The lack of success in performing proton-spin alignment in frozen aqueous solutions of ytterbium chloride (Lichti and Stapleton, 1973) even though there exists a Stark splitting, may be a consequence of the width of the levels, if the width of the fundamental Stark level is homogeneous and is of the same order of magnitude as that of the excited levels.

The results obtained from this work and related work done with other rare earths do not at present permit us to determine the exact nature of the phase responsible of the observed spectra, but we can limit the possibilities and infer what is most probable.

The number of lines for neodymium chloride solutions (Couture and Le Paillier-Malécot, 1975) indicate that there exists only one type of site for the rare-earth ions. Also the splitting
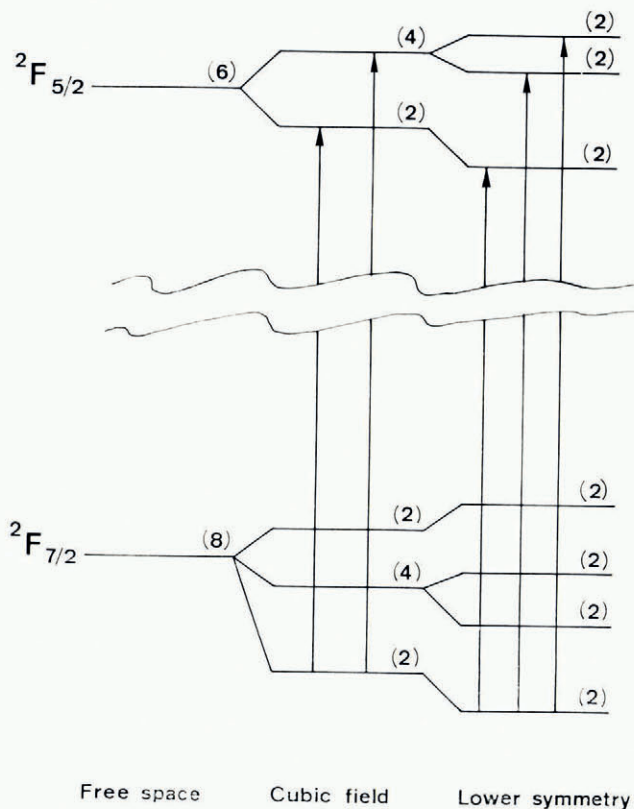

Fig. 2. *Schematic energy levels of an ytterbium Yb^{3+} ion in various surroundings.*

of the excited $^4F_{3/2}$ level of neodymium completely rules out the possibility of cubic symmetry at the site of Nd^{3+} ions, although it is consistent with any site symmetry lower than cubic.

The absorption spectra of frozen ytterbium chloride aqueous solution strongly differs from that of ytterbium chloride hydrated crystal $YbCl_3 \cdot 6H_2O$ both in frequencies and widths of the lines. The same thing occurs with frozen solutions of other salts. The absorbing phase is then not one of the known crystalline hydrated chlorides.

Frozen aqueous solutions of neodymium chloride with and without HCl give the same spectra. The possibility of having a crystal containing hydrogen chloride has thus to be ruled out.

The Stark splittings observed in the spectra of frozen aqueous solutions of ytterbium chloride can then be accounted for by the following two possibilities. A vitreous solution of $YbCl_3$ in water may present a quasi-crystalline order in the immediate vicinity of the rare-earth ion, with a quasi-symmetry lower than cubic; the widths of the lines could in this case be accounted for by inhomogeneities of the field. Hexagonal Ih ice may have definite sites occupied by ytterbium ions, thus forming a crystalline solid solution; this could explain easily the high-pressure observations (Jean-Louis and Couture, in press), but the reason for the width of the lines should be found, possibly proton disorder in ice is responsible.

CONCLUSION

The absorption spectrum of frozen aqueous solutions of ytterbium chloride is essentially independent of temperature between 4 K and 77 K and shows characteristic line widths greater than the line widths of rare-earth ions in crystals at low temperature and with similar concentration, and less than the widths for liquid solutions.

A splitting of 60 cm^{-1} in the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition is observed, identified as a splitting of the excited $^2F_{5/2}$ state and attributed to the Stark effect arising from a local quasi-crystalline or a crystalline environment of cubic or lower than cubic symmetry; however, related experiments on frozen aqueous solutions of neodymium chloride show that the symmetry of the surroundings of neodymium is lower than cubic.

ACKNOWLEDGEMENTS

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DISCUSSION

S. A. RICE: Is it not likely that when you freeze the solution of YbCl$_3$ the Yb^{3+} ion is incorporated *along with* its water of hydration? It is known that the rate of exchange of water in the hydration shell of a trivalent ion is very small; a half-life of a day is not unusual. If this conjecture is correct your experiment does not probe the environment of ice Ih, but of a hydrated ion crammed into an ice Ih lattice, with distortion of the hydration sphere by the surrounding lattice. Perhaps the hydration sphere can conform to the lattice, perhaps not. It is likely that the line widths for electronic transitions will be smaller than in a fluid solution (as in the Shpolski effect), and perhaps at sufficiently large pressure the original shell is distorted and even destroyed. It is also possible that your solid is heterogeneous and the Yb^{3+} is not incorporated substitutionally. Some check on the structure will be needed to check your suggested interpretation.

L. COUTURE: The presence of water of hydration cannot be excluded. Those spectra show that Yb^{3+} ions are in definite sites, but not what sort of sites.

A. P. MACKENZIE: It seems to me that many, possibly all your findings are best explained on the basis of a freezing out of pure ice Ih from an initially dilute (*c.* 1% w/w) solution, and the generation of a concentrated amorphous phase might reach 50 to 75% w/w YbCl$_3$ and fail to yield a eutectic, persisting instead in a truly amorphous condition. Experience with the freezing of di- and trivalent cation salt solutions in a number of laboratories suggests the frequent reluctance of the salts to crystallize in practice. Such a physical mixture of ice and concentrated amorphous aqueous salt would satisfy your requirement that each Yb^{3+} ion occupy an essentially like site. Each Yb^{3+} ion could maintain some water of hydration. Cl$^-$ ions would, similarly, persist in the same amorphous phase. What do you think of the possibility?

COUTURE: I do not exclude this possibility. But why should the spectra disappear and reappear with the Ih ice phase? And phases with a high concentration in rare-earth ions do not show any fluorescence.