IV. Spectra of Ions in Crystals and Solutions

Spectra of Ions in Fields of Various Symmetry in Crystals and Solutions

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INTRODUCTION

A SIGNIFICANT beginning in our knowledge of the influence of fields of the environment upon the spectra of ions was made early in spectroscopy by Bunsen.[1] He observed different absorption spectra from crystals of didymium sulfate octahydrate depending upon the orientation of the crystal with respect to the light. In a given crystallographic direction he found the spectra different with light polarized in different orientations. H. Becquerel[2] made a thorough study of this phenomenon with many minerals, most of them containing rare earths. Because of the sharpness of their bands, the appearance and disappearance of structure could be recognized more definitely than the partial changes in the diffuse bands of other substances. About twenty years later and from then on until the most recent times, J. Becquerel[3] examined the spectra of some of these minerals and other substances at low temperatures and found a striking refinement of bands into sharp lines. In the course of his investigations, he discovered a Zeeman effect from these crystals and became especially interested in their magnetic rotation. Kramers[4] undertook an interpretation of these experiments by means of quantum theory and arrived at a number of important results—one especially significant that the electrical fields of the lattice do not remove the degeneracy coming from spin of the electrons. Even before this, Bethe,[5] employing group theory, laid the groundwork for the study of energy states in crystals. He derived the number and symmetry characteristics of the component levels which arise from a given energy level of an atom after it is embedded in fields of various crystallographic symmetries. At the same time, he treated the problem for different intensities of coupling between the lattice and the electronic motions in the atom—from one extreme interaction when the electric fields of the lattice couple with the orbital momentum of an electron more tightly than the orbital momenta of the electrons couple with each other to the other extreme, when the interaction with the lattice is weaker than the coupling between the net orbital momentum and the net spin momentum of the electrons within the atom. In this instance, the energy intervals induced by the lattice are small compared with the spacings within a given multiplet and the coupling of the electrons in the gaseous atom remains intact inside the crystal.

Examples of strong interaction with the lattice occur in crystals containing ions of the transition elements such as in the iron group. Van Vleck,[6] Penney, and their co-workers have carried out many theoretical investigations on the magnetic behavior of these ions, taking the interactions with the crystalline fields into account.

The ions of the rare earths conform rather closely to the case of weak coupling with the lattice because of the shielding afforded the electrons of the incomplete $4f$ shell by the filled $5s$ and $5p$ shells. The ions in the lattice may then be regarded as having the same total angular momenta as in the gaseous state now oriented by the fields of the lattice. Not only is the perturbation on known situations in the gas less intense among the rare earths than, say, among the ions of the iron group but the special sharpness of their spectra permit the evaluation of energy levels by methods so successfully employed with gases.

The basic states of the rare earth ions in crystals and solutions were established by Hund[7] in seeking to confirm his rule for the quantum character of the basic state of ions in gases. He turned to paramagnetic susceptibilities since these are primarily properties of the basic state and his computed values for the gaseous atomic ions were practically equal to the measured magnitudes for the ions in crystals and solutions.[8] There were, however, several apparent deviations both from the theory and ideal magnetic behavior, notably with the salts of samarium. However, the absorption spectra[9] revealed temperature sensitive lines, that is, energy levels comparable with

kT, even near room temperature. These for the most part represent the decomposition of the basic state by the crystalline field, the phenomenon we shall chiefly discuss here. Similar deviations are shown by other rare earths at low temperatures.[10] At higher temperatures the average over all the crystalline levels gives the theoretical behavior for gaseous ions.

In Table I are reproduced the numbers of components which Bethe derived for a succession of quantum states in fields of crystallographic symmetries. There still appear to remain some discrepancies between these numbers and those obtained experimentally, especially with samarium. From constant intervals in the absorption spectrum, Spedding and Bear have deduced at least four low lying levels and the table shows that the maximum is three. Heat capacity measurements[11] which give the energies of activation into levels close to the ground state are in good agreement with the four levels. Nevertheless, it could scarcely be doubted that the group theoretical results of Bethe are at least a proper qualitative description of the situation in crystals. Certainly the conclusion that in more symmetrical fields, there will in general be fewer component levels is in accord with evidence that, as a rule, fewer lines appear within corresponding groups in more symmetrical crystals.[12] However, it is the local symmetry about the rare earth ions which determines the degree of splitting rather than the macroscopic symmetry of the crystals.

TABLE I. Number of component levels induced by crystalline fields.

Symmetry of field	$J=0$	1	2	3	4	1/2	3/2	5/2	7/2
Cubic, octahedral	1	1	2	3	4	1	1	2	3
Hexagonal	1	2	3	5	6	1	2	3	4
Tetragonal, rhombic, and less symmetrical	1	3	5	7	9	1	2	3	4

A quantitative test of the theory with known microscopic fields was made possible with the results Gobrecht[13] obtained in his study of the structure of the infra-red fluorescence spectra. Of especial interest were his spectra of the ions in the last three rows of Table II (which should be read down on the left and up on the right). Terbium, immediately after gadolinium, has for its basic state a septet level ^7H. On irradiating terbium salts with resonance radiation, Gobrecht observed in fluorescence seven separated groups of lines. The intervals between successive groups were greater toward shorter wave-lengths and the number of lines within each group increased in the same order. Both of these facts point directly to the conclusion that all the groups of lines originate in the same excited level and end in the seven levels of the basic multiplet ^7H. Each of the levels has become a group induced by the crystalline fields and since the term is inverted as the atom comes after gadolinium (the $4f$ shell half-full) there are more lines in the groups at shorter wave-lengths. Furthermore, the interval rule calls for greater separations between lines having greater values of J. This conclusion is further strengthened by the structure of the spectra from the ions before gadolinium. Here the intervals between the groups in fluorescence become more closely spaced toward shorter wave-length, in agreement with the fact that the multiplet is direct, i.e., the level having the lowest value of J is the most stable. Because of the simple regularity in the fluorescence spectra, Gobrecht was in position (especially with europium) to assign quantum numbers to the states between which transitions occurred, in absorption as well as in emission. One specific consequence of this assignment was to rule out as incorrect the assumption that the electric fields about the ions of the rare earths in the sulfate octahydrates were of cubic symmetry. The transition in J 0→1 consisted of a group of three lines but it should have consisted of one at most if cubic symmetry obtained about the Eu^{+++}. Van Vleck, Penney, and others in their computation of the paramagnetism of these had supposed on the basis of previous analyses of the spectra that the fields were cubic with perhaps a slight orthorhombic perturbation. This approach has led to an impasse, apparently.[14]

TABLE II. Basic states of ions of the rare earths.

Ions	Basic state	(5s, 5p shells full) No. of electrons in 4f shell		Basic state	Ions
La^{+++}	$^1S_0$	0	14	$^1S_0$	Lu^{+++}
Ce^{+++}	$^2F_{5/2}$	1	13	$^2F_{7/2}$	Yb^{+++}
Pr^{+++}	$^3H_4$	2	12	$^3H_6$	Tu^{+++}
Nd^{+++}	$^4J_{9/2}$	3	11	$^4J_{15/2}$	Er^{+++}
Il^{+++}	$^5J_4$	4	10	$^5J_8$	Ho^{+++}
Sn^{+++}	$^6H_{5/2}$	5	9	$^6H_{15/2}$	Dy^{+++}
Eu^{+++}	$^7F_0$	6	8	$^7F_6$	Tb^{+++}
Gd^{+++}	$^8S_{7/2}$	7			

EXPERIMENTS WITH CRYSTALS

It now seemed possible to test the applicability of Bethe's theory to crystals.[15] The anhydrous fluorides of the rare earths are hexagonal with the local symmetry C_{2v} about the rare earth ions. Such a symmetry would, according to theory, remove all the degeneracy of the levels in Eu^{+++}. Any level of given J will decompose into $2J+1$ levels. In accordance with Gobrecht's assignments which have also been found consistent with many spectra taken in this laboratory, the group of lines at 4650A is a transition $0 \rightarrow 3$, the group at 5250A is $0 \rightarrow 2$, and at 5780A, the single line is a $0 \rightarrow 0$ transition. In a field of symmetry C_{2v}, $J=3$ is split into seven states, $J=2$ into five and $J=0$ must remain single. With this set of numbers the lines found in the absorption spectrum were in full agreement, seven lines in the groups at 4650A (see Fig. 1), five at 5250A, and one at 5780A.

It is also possible to have EuF_3 in a cubic lattice. Bismuth fluoride BiF_3 is cubic, with the local symmetry cubic holohedral O_h about Bi^{+++}. It has long been known among chemists that many bismuth salts are isomorphic with the corresponding salts of the rare earths and their miscibility in crystals has played an important role in the separation of the rare earths from each other. Mixed crystals of bismuth and europium fluorides with the bismuth salt in great preponderance were in fact found to remain cubic. The europium ions occupied positions at the center of holohedral O_h symmetry to a high degree of approximation. As in the hexagonal crystal, fluoride ions constituted the first coordination zone about the europium ion and the more remote zones were occupied by bismuth ions, similar to the europium ions in the more remote zones of europium fluoride. According to Table I, the $0 \rightarrow 3$ transition should now consist of three lines instead of the seven in the spectrum of the hexagonal crystal; the $0 \rightarrow 2$ groups should contain two lines and the $0 \rightarrow 0$ but one. (See Fig. 1.) This was the precise number of lines actually present in the respective groups.

EXPERIMENTS WITH SOLUTIONS

Solutions of salts of europium possess spectra closely resembling the spectra from crystals. The spectra are of exceptional sharpness compared with spectra from other solutions. It appeared possible then that the spectra might be sharp enough to register different numbers of lines in the groups when the environment about europium ion was changed, and we would have the same general theoretical basis to guide the interpretations for solutions as for crystals. This anticipation was actually fulfilled.[16] For example, a solution of europium chloride in water had a structure in the $0 \rightarrow 3$ group of three rather closely spaced lines and one somewhat further removed toward longer wave-lengths, with the two inner lines somewhat diffuse, whereas the aqueous solution of europium nitrate had three sharp lines almost equally spaced. (See Fig. 2.) When a solution of europium nitrate in ether was examined, its spectrum consisted of but two lines in this group.

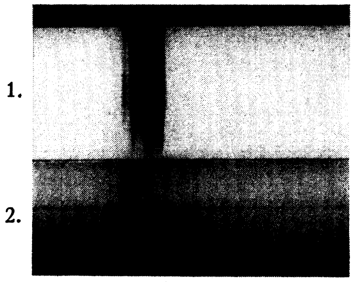

FIG. 1. The group at 4650A, fourfold enlargement (increasing λ to right). 1. Seven lines from crystal EuF_3; local symmetry C_{2v} about Eu^{+++}. 2. Three lines from cubic mixed crystal $Bi-EuF_3$; local symmetry O_h about Eu^{+++}.

The first measurements had been made with solutions from 1.5 molal to about 0.01 molal in the salts and the patterns of the chloride and of the nitrate in the spectrum remained unchanged despite the fact that these salts are strong electrolytes. A 0.01-molal solution of europium nitrate has a freezing point lowering from that of pure water about three and one-half times as much as is produced by the same concentration of a non-electrolyte such as sugar. Because of the great similarities in the thermodynamic properties of the rare earths, the complete miscibility in the solid state, etc., it has been assumed from the start that europium ion may be regarded as an indicator for the fields about the other rare earth ions and in many instances about other trivalent ions. For this reason it seemed very

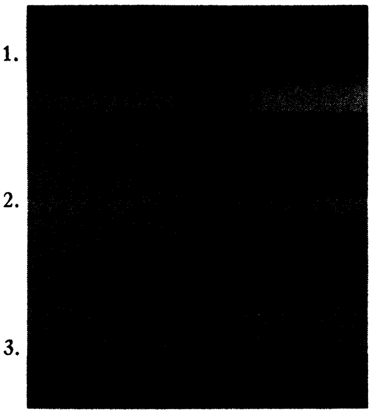

FIG. 2. The group at 4650A, fourfold enlargement (increasing λ to right). 1. Four lines from $EuCl_3$ dissolved in water. 2. Five lines from $EuCl_3$ solution to which KNO_3 was added. Superposition of four lines of europium chloride and three lines of $Eu(NO_3)_3$ two of which overlap. 3. Three lines of $Eu(NO_3)_3$ dissolved in water.

likely that the many thermodynamic data on salts of lanthanum (the "model" trivalent ion)[17] are a fairly close approximation for the data of the corresponding salts of europium. The freezing point data above quoted were actually obtained with lanthanum nitrate.[18] To put all scepticism at rest, Klotz[19] measured the electrical conductances of aqueous solutions of europium chloride and europium nitrate and obtained values very close to the published data on the corresponding salts of lanthanum. The difference between the equivalent conductances of the chloride and the nitrate was of the same order of magnitude as the differences between those of potassium chloride and potassium nitrate.

We are then actually faced with the fact that the spectra of solutions reveal different discrete structures in the fields about the ions when their environment is altered. Upon further dilution, the spectrum of the chloride remained unchanged down to about $0.0003M$, but from the nitrate a new spectrum made its appearance at about $0.01M$.[20] It was indistinguishable from the chloride spectrum and as the dilution continued, it gained in relative intensity at the expense of the nitrate spectrum. Even at $0.0007M$ the coexisting spectra were unchanged as to wave-length, but the nitrate spectrum had almost disappeared. Other negative ions such as sulfate, acetate, also had their characteristic effects in the spectra but many of the common negative ions behaved like the chloride ion. When potassium nitrate was added to a solution of europium chloride, there appeared a sharp superposition of the same two spectra[21] (Fig. 2). The europium ions had distributed themselves between two configurations corresponding to the chloride and nitrate structures. Since the nitrate had displaced the chloride ions from the environment of some of the europium ions, a program presented itself: to determine the relative ionic affinities of the negative ions for positive ions under these conditions. Even those ions which resemble the chloride ions in their effect on the spectroscopic structure will probably respond unequally to displacement by a given negative ion. Correspondingly, there exist relative ionic affinities of positive ions for negative ions, e.g., different quantitative relations are to be expected when thorium nitrate instead of potassium nitrate is added to the solution of the chloride. A similar distribution of europium ions between different configurations in homogeneous solutions takes place in mixtures of various solvents. Europium chloride in absolute alcohol gives a markedly different spectrum from that in water (Fig. 3). When a small amount of water is added to the alcoholic solution, the "hydrate spectrum" appears accurately superimposed on the "alcoholate-spectrum" and also with more water it grows in intensity at the expense of the latter. Finally at about 20 percent water the alcoholate-spectrum is entirely displaced. Europium nitrate in absolute alcohol shows a different behavior when water is added. Not only does the hydrate-spectrum of the nitrate make its appearance but the positions of the lines shift at higher concentrations of water. The lines remain sharp, however, and the spectrum from the salt in a mixture of solvents is a sharp average as regards position and not a blur between the two limiting spectra of the salt when in the separate pure solvents.

COUPLING WITH GROUP AND LATTICE OSCILLATIONS

H. Ewald[22] discovered that when the absorption spectrum of a neodymium salt, e.g., $3Mg(NO_3)_2 \cdot 2Nd(NO_3)_3 \cdot 24H_2O$, is taken through a thick layer at the temperature of liquid hydrogen, the strong groups of lines characteristic of Nd^{+++} are accompanied at shorter wave-lengths by faint repetitions of their patterns. Intervals between the groups and their repetitions are the same throughout the spectrum. These frequency differences agree closely in magnitude with the well-known vibrational frequencies of the constituent ions and molecules in the lattice—in the particular mixed nitrate cited, with the vibrational frequencies of nitrate ion and also of water. When heavy water replaced ordinary water of crystallization, the intervals diminished to the proper frequencies of heavy water. In addition to these modulated frequencies, Ewald observed faint groups of lines closer to the main electronic transitions, which also moved toward the intense groups when heavy water was substituted for light water and when zinc ion replaced magnesium ion in the crystal. He concluded that these low frequencies, from 50 cm^{-1} about 200 cm^{-1}, represented lattice vibrations coupling with the electronic frequencies, since an increase in mass of the lattice atoms effected a decrease in the frequencies. Substantiation was obtained by Hellwege[23] by direct measurement with reststrahlen.

These experiments were repeated[24] with the corresponding salts of europium, but the sharpness of the spectrum permitted that the crystals remain at room temperature. Ewald's results were confirmed. In addition, however, to the lattice oscillations on the short wave-length side of the electronic frequencies, there appeared a similar pattern of lines toward long wave-lengths displaced an equal amount in frequency. When the temperature of the crystals was lowered with liquid air, these new lines vanished as one group. Clearly, they were active thermal oscillations of the lattice and their presence in the spectrum corresponded to anti-Stokes frequencies in the Raman effect. The magnitudes and the number of the lattice vibrations coupling with the electronic transition varied from salt to salt.

When the europium salts were dissolved in water to make rather concentrated solutions, similar repetitions of the main groups were present in the spectrum of the solution. Also occurring on both sides of the strong groups, they were more diffuse than in crystals and usually somewhat different in magnitude, varying also with the salt and the solvent. In alcoholic solution they were sharper than in aqueous solution, in keeping with the regularities which x-ray diffraction experiments have shown in alcohol. And in more dilute solutions in water the vibrational structure appeared more diffuse.

At first the tendency is to think of the oscillations corresponding to lattice oscillations in crystals as originating in complexes constituted by the water molecules in the first coordination zone about the europium ions. Such a limited zone can scarcely account for these oscillations in view of the following facts: (1) The ionic crystal of europium fluoride $\mathrm{EuF_3}$ with its long-range forces extending throughout the lattice also exhibits these lattice oscillations. The crystal structure which has been derived from x-ray data allows for no clusters of particles in the lattice. In agreement with this view is the magnitude of these lattice frequencies, about twice as high as any observed from crystals containing water of crystallization, and hence consistent with the tightness of the ionic binding. (2) It has already been stated that when as much as 20 percent water is added to a solution of a europium salt in absolute alcohol, the main electronic frequencies are identical with those from the salt in pure water. The alcoholate-spectrum had been entirely displaced. However, the quasi-lattice vibrations present include both those from a solution in pure water and those from the solution in absolute alcohol. (3) The coordination compound europium acetylacetonate dissolved in benzene, despite

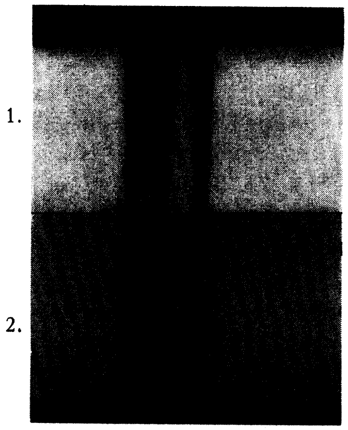

FIG. 3. The group at 4650A, sixfold enlargement (increasing λ to right). 1. $\mathrm{EuCl_3}$ in absolute alcohol. 2. $\mathrm{EuCl_3}$ in 200 cc absolute alcohol to which 0.45 cc water was added.

very intense absorption of the electronic frequencies, did not show any trace of the quasi-lattice vibrations. Yet this might have been imagined as an excellent cluster for such oscillations. In it the europium is coordinated to three pairs of oxygen atoms between which are chains of carbon which in turn have hydrogen atoms attached. There was, however, some sign of such a vibration when the acetonate doubled to form the dimer.

Although it is too early to be definite as to how far from the europium ions the oscillating units need be assumed to extend in a good approximation, it seems that they extend farther than most of us are prepared to accept at present.

WIDE-ANGLE INTERFERENCE EXPERIMENTS

There is another method available for deriving information on the symmetry of the fields about ions in solution, namely the method of wide-angle interference of radiation.[25] The properties of the interference fringes depend on the multipole character of the radiation which emanates from fluorescence centers in solution. A particular species of radiation can, in general, be emitted in a given quantum transition on condition that certain symmetry elements are absent in the fields about the emitting ions.

Three groups of lines in the fluorescence spectrum of europium have been unambiguously assigned by Gobrecht to the following J transitions: 0→0, 0→1, 0→2. None of these transitions, since both initial and final states have their electronic configurations within the $4f$ shell,[26] can occur as dipole radiation in gases or in a field having a center of symmetry. The selection rule (Laporte's rule) does not exclude the radiation if the field lacks a center of inversion. Furthermore, on grounds of rotational symmetry the 0→2 may not occur as dipole radiation in regions having spherical symmetry, but quadrupole radiation would be allowed. On the same basis, the 0→1 transition is allowed both as electric or as magnetic dipole radiation in spherically symmetrical fields, while the 0→0 transition is excluded for all radiation arising in such an environment. The behavior of the fringe systems from europium salicylaldehyde established that the 0→0 and the 0→2 transitions consisted of electric dipole radiation. (Fig. 4.) The first of these transitions is consistent with an electric field at least as unsymmetrical as C_3 and the second with either a hexagonal, tetragonal, or a less symmetrical field, but these by the first condition must lack also a center of symmetry. The 0→1 transition proved to be magnetic dipole radiation, and this is permitted in any of the symmetries consistent with the other two radiations. It follows that the fields about the fluorescent ions have at most the symmetry C_3.

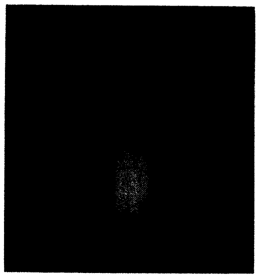

FIG. 4. Wide-angle interference of fluorescence radiation. Three groups of lines 5790A, 5880A, 6100A from europium salicylaldehyde in pyridine. 1. The 5790A and 6100A groups exhibit distinct interference fringes and the 5880A group does not. 2. On rotating a polarizing prism 90°, the situation is reversed—the 5880A group consists of interference fringes and the others do not. Conclusions are that the group at 5790A and at 6100A are electric dipole radiation while the group at 5880A is magnetic dipole radiation. Since quantum transitions are known, absence of certain symmetry elements in the local environment of the ion is established.

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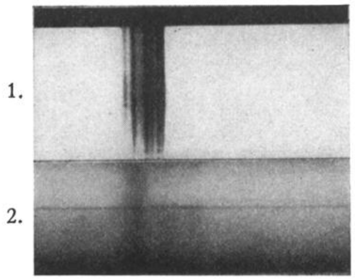

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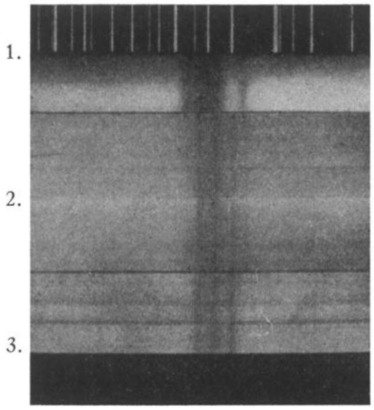

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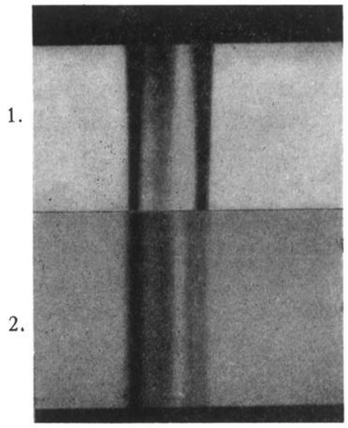

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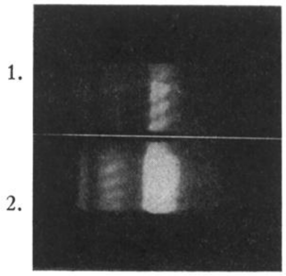

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