# THE PUZZLE OF RARE-EARTH SPECTRA IN SOLIDS<sup>1</sup>

J. H. VAN VLECK

Research Laboratory of Physics, Harvard University, Cambridge, Massachusetts

Received October 6, 1936

It is well known that crystals of rare-earth salts are often characterized by sharp absorption or emission lines. The understanding of the precise nature of these lines, i.e., their spectroscopic classification and pedigree, is a matter of considerable interest to chemists and physicists, since these lines are intimately associated with the binding of the rare-earth atoms in the solid state, and so their analysis may provide us with information on crystalline forces. Such study is, of course, to be distinguished from that of gaseous atomic spectra, which tell us nothing about interatomic forces. Any acceptable interpretation of rare-earth solid spectra must be compatible with two other lines of evidence: (a) magnetism and (b) specific heats. The reconciliation of the different facts is far from easy, and so I have referred to the entire subject as a "puzzle" as far as existing knowledge is concerned. Practically all rare-earth salts are trivalent, so that all our questions relate to the behavior of the trebly ionized atom in solids.

It is now generally conceded, I believe, that the ground states of the trivalent rare-earth ions are of the form  $4f^x$ , where x = 1 for Ce<sup>+++</sup>, 2 for  $Pr^{+++}$ , ... 13 for Yb^{+++}. Besides the very definite magnetic evidence to this effect, the recent beautiful spectroscopic work of Lang (13) shows conclusively that the ground state of the free Ce<sup>+++</sup> ion is  $4f^2F_{5/2}$ , despite the fact that extrapolation by the irregular doublet law from the less Thus we can regard it as enhanced spectra would appear to favor 5d. definite that the lower level in rare-earth absorption belongs to  $4f^x$ . The classification of the upper level is more of a question. There are two possibilities, which I shall term respectively the excitation and non-excitation In the former, the upper state belongs to a different conhypotheses. figuration from the ground state, and is presumably often of the form  $4f^{x-1}5d$  or  $4f^{x-1}5g$ . In the non-excitation hypothesis, on the other hand, the upper state belongs to the same configuration,  $4f^x$ , as does the ground state, and differs from it only in the value of the collective azimuthal

<sup>&</sup>lt;sup>1</sup> Presented at the Symposium on Molecular Structure, held at Princeton University, Princeton, New Jersey, December 31, 1936 to January 2, 1937, under the auspices of the Division of Physical and Inorganic Chemistry of the American Chemical Society.

quantum number L or in the spin S, the individual l's being the same. With the excitation hypothesis, the transition is due to ordinary dipole radiation, whereas with the non-excitation hypothesis, we have to deal with a forbidden transition, which is not allowed by the Laporte selection rule (that the algebraic sum of the individual l's must change by an odd integer (6)), but which is allowed with faint intensity if one considers quadrupole or magnetic dipole radiation, or distortion by crystalline fields. In my opinion the non-excitation hypothesis advocated by Freed (10), Tomaschek (23), and others, is the correct one in the case of the *sharp* lines, for the reasons given below.

# EVIDENCE THAT THE RARE-EARTH LINES REPRESENT FORBIDDEN TRANSITIONS

According to this hypothesis, sharp lines should not be found for salts involving cerium or ytterbium, since the configurations 4f and  $4f^{13}$  each yield one value of L, and hence one orbital level, whereas two are needed, namely, an upper and a lower level. Actually the sharp lines are missing for both the cerium and ytterbium salts. This argument has been particularly stressed by Freed (10). Of course, lines due to excited configurations should still be permitted in cerium and ytterbium, but the excited states reside on the outside of the atom, and are not sheltered from disturbing interatomic forces. Hence it is commonly supposed that they can have broad, diffuse Stark effects, and indeed intense diffuse absorption bands are found in cerium and ytterbium salts in the ultra-violet, ascribable (10) to excitation of an electron to 5d.

A second argument is furnished by considerations of intensity. At first thought one might opine the contrary, as forbidden lines are often undetectable in gaseous spectra. However, we are dealing with the solid, the high density of which enhances the intensity by a factor a million or more, and so even feeble violations of the selection principle should give rise to perceptible radiation. Actually, the measurements of Becquerel (3) and others (23, 11) reveal in  $Pr^{+++}$  and  $Nd^{+++}$  an intensity about a millionth as great as one would expect for ordinary dipole radiation. Also it is particularly striking that in  $Pr^{+++}$  and  $Nd^{+++}$  the sharp lines in the visible do not show up at all as resonance centers in rotary dispersion, showing that their intensity is exceedingly low (11, 17). Instead the dependence on wave length is so slight that the strong centers due to 4f-5d must be far out in the ultra-violet.

We must, however, mention that the opposite interpretation, the excitation hypothesis, is maintained by Spedding (21). His most telling argument is perhaps that chromium and other salts of the iron group show sharp structures despite the fact that here the 3d electrons are to a considerable extent on the outside of the atom, and so not sheltered from interatomic fields. Hence mere sharpness does not imply interior location of the orbit. A possible, though admittedly only conjectural, answer is that the spectroscopic manifestations of the coupling between vibration and electronic motion may be more complicated when there is a change in electron configuration. In diatomic spectra, for instance, electron bands show much more prolific vibrational structure than do vibration bands in which the electron structure does not change. Conceivably there is a similar situation in the complexes found in solids. The sharp lines in chromium, etc., are due to forbidden transitions  $3d^3 - 3d^3$  not involving a change in electron configuration, and so could be sharp according to this idea.

# POSSIBLE CAUSES OF NON-VANISHING INTENSITY FOR THE FORBIDDEN TRANSITIONS

Why should the forbidden lines be visible at all, faint though they may be? There appear to be the following alternative explanations: (I)



FIG. 1. In IIIa, the potential curve is unsymmetrical with respect to the equilibrium position O of the nucleus. In IIIb, there is symmetry with respect to the nucleus as origin if it is at O, but not if vibration carries it to some other point P.

quadrupole radiation; (II) magnetic dipole radiation; and (III) electric dipole radiation, caused by distortion of the electronic motion by the crystalline fields, so that the selection rules for the free atom no longer apply. III differs in this respect from I and II, as I and II are effects characteristic even of free atoms. Not all crystalline fields are adequate to produce III. It is necessary that the field not have a center of symmetry, i.e., not be holohedral, as otherwise the wave functions would retain their even-odd classification as regards reflection in the origin, and the Laporte rule that only even and odd terms can combine (i.e., that  $\Delta \Sigma_i l_i$  must be an odd integer) would remain rigorous. Even if there is a center of symmetry at the equilibrium position, obviously this property is lost when the atom starts vibrating, as is shown in figure 1. One can therefore distinguish between the two following forms of III: (IIIa) The crystalline field does not have a center of symmetry even at the equilibrium position; (IIIb) The departures from holohedral symmetry are due entirely to atomic vibration.

It is of interest to ascertain whether I, II, IIIa, or IIIb is the proper

explanation, as information is thereby communicated as to the nature of the interatomic forces, vibrational coupling, etc. Perhaps all the causes enter at the same time, and the spectrum is obviously then of great complexity. One would like a detailed x-ray analysis of the positions of the individual atoms in the rare-earth crystals, as this would definitely tell us to what extent the crystalline field has a center of symmetry at the equilibrium position of the rare-earth atoms. Unfortunately, it appears impossible to obtain this information, as x-ray experimentalists cannot locate the hydrogen and oxygen atoms because of their light masses. In the case of  $Sm_2(SO_4)_3 \cdot 8H_2O$ , Zachariasen (25) has located the position of the samarium atoms by x-ray analysis, and their arrangement is such that there cannot be holohedral symmetry as far as the part of the crystalline field due to Sm-Sm forces is concerned. However, this is not the important part, as the samarium atoms are at large distances from each other because of the intervening waters of hydration. More important are the forces due to nearby oxygen atoms, and conceivably they may be grouped with nearly perfect cubic symmetry. Crystals like  $Sm_2(SO_4)_3 \cdot 8H_2O$ , to be sure, belong to the monoclinic system, for which a center of symmetry is not to be expected, but this fact does not preclude the symmetrical clustering of oxygen atoms about the samarium atom. It is thus conceivable that the hemihedral portion of the crystalline field results entirely from distant atoms and is of subordinate importance.

It is sometimes convenient to expand the crystalline potential  $V_{\text{crys.}}$  in terms of the displacement  $x_i$ ,  $y_i$ ,  $z_i$  of a typical 4f electron from the equilibrium position of the nucleus, so that

$$V_{\text{crys.}} = \Sigma_i \{ A_0 + A_1 x_i + B_1 y_i + C_1 z_i + A_2 x_i^2 + B_2 x_i y_i + C_2 y_i^2 + \dots + A_3 x_i^3 + \dots + A_4 x_i^4 + B_4 x_i^3 y_i + \dots \}$$
(1)

or in polar coördinates

$$V_{\text{crys.}} = \Sigma_i \{ A_0 + r_i f_1(\theta_i, \varphi_i) + r_i^2 f_2(\theta_i, \varphi_i) + r_i^3 f_3(\theta_i, \varphi_i) + \cdots \}$$
(2)

where the summation is to be taken over all of the 4f electrons in the atom. The expression 1 or 2 is a sort of Hartree potential for the electron, except that now the field is due to the entire crystal rather than simply the single atom itself. If the field has a center of symmetry, the odd powers in rare absent.

## ALLOWED TRANSITIONS

The transition probability for ordinary electric dipole radiation is (4)

$$\sigma = 64\pi^4 e^2 \nu^3 q^2 / 3hc^3 \tag{3}$$

where  $\nu$  is the frequency of the radiation in question, and q is the matrix amplitude for the transition. If it is an allowed one,  $q^2$  is of the order of magnitude of the mean square radius  $r^2$  of the orbit, given by

$$r^2 = \iiint \psi^2 r^2 dv \tag{4}$$

To estimate the expression 4, we use a 4f wave function

$$\psi = Ar^3 e^{-Zr/4a_0}$$

for a hydrogenic atom of effective charge Ze. Here  $a_0$  has its customary significance

$$a_0 = h^2/4\pi^2 e^2 m$$

The value of Z is to be so determined as to yield the proper binding energy. This energy is known for the 4f state only in Ce<sup>+++</sup>, where (13) it is 296,197. cm.<sup>-1</sup> The corresponding value of Z is 6.6, and equation 4 yields

$$r = (360 a_0^2 / Z^2)^{\frac{1}{2}} = 1.53 \times 10^{-8} \text{ cm.}^{-1}$$
 (5)

If  $\nu$  is 20,000 cm.<sup>-1</sup>, the approximate value for visible light, one then has

$$\sigma = 1.3 \times 10^8 \text{ sec.}^{-1} \tag{6}$$

We now proceed to estimate the rough magnitude of the transition probability  $\sigma$  for various types of forbidden transitions.

## FORBIDDEN TRANSITIONS

## I. Quadrupole radiation

For a quadrupole transition, the expression which replaces expression 6 is (4)

$$\sigma_{\rm I} = 32\pi^6 \nu^5 e^2 Q^2 / 5hc^5 \tag{7}$$

Here Q is the "quadrupole amplitude", which is comparable dimensionally with the mean square radius of the orbit. However, the numerical factors which cannot be estimated from dimensional considerations are more important than in the dipole case. Namely, examination of the more precise formulas for Q given, for instance, in Condon and Shortley's<sup>2</sup> book shows that for a  $4f \rightarrow 4f$  transition,  $Q^2$  is usually considerably smaller than  $r^4$  as defined in equation 4, and is sometimes even less than  $r^4/100$ . We shall therefore for our qualitative purposes take

$$Q^2 = r^4 / 10 \tag{8}$$

Then if  $\nu = 20,000$  cm., expression 7 becomes

$$\sigma_{\rm I} \sim 4 \, \, {\rm sec.}^{-1} \tag{9}$$

<sup>2</sup> Reference 4, pp. 252-5; the important fact is that on p. 255 the quantity G of Condon and Shortley is considerably smaller than their  $S_2/e$ , which corresponds to our  $r^2$ .

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#### II. Magnetic dipole radiation

Besides ordinary electric dipole radiation, there can also be magnetic dipole radiation (5), which, unlike the former, connects states of similar Laporte symmetry. The resulting transition probability is

$$\sigma_{\rm II} = 64\pi^4 \nu^3 M^2 / 3hc^3 \tag{10}$$

where M is the matrix element of the magnetic moment connecting the states in question. If we neglect spin-orbit interaction, the matrix elements M will vanish except between components of the same multiplet, whereas we require them to exist between different multiplets. For example, in  $Pr^{+++}$  there are elements joining  $f^{23}H_4$  and  $f^{23}H_5$ , but not  $f^{23}H_4$  and  $f^{21}G_4$ . There will, however, be elements of the desired type if we allow for spin-orbit interaction, which prevents L and S from being rigorously "good quantum numbers". The resulting values of M are of the order of magnitude  $\alpha\beta$ , where  $\beta$  is the Bohr magneton  $he/4\pi mc$ , and  $\alpha$  is the portion of the wave function which is of extraneous L or S. The order of magnitude of  $\alpha$  is  $\Delta \nu / \nu$ , where  $\Delta \nu$  is the multiplet width and  $\nu$  is the interval between different multiplets. A reasonable estimate of  $\alpha$  seems to be 1/10, as  $\Delta \nu$  is between 1000 and 10,000 cm.<sup>-1</sup>, while  $\nu$  is between 10,000 and 100,000 cm. $^{-1}$  Then expression 10 becomes

$$\sigma_{\rm H} \sim 2 \; {\rm sec.}^{-1} \tag{11}$$

Comparison of expressions 9 and 11 shows that there is not much difference in the importance of quadrupole and magnetic dipole radiation. The situation is thus quite different from that in light atoms like oxygen, where the magnetic radiation is less significant because the spin-orbit interaction is much smaller than in the rare earths (5).

# III. Electric dipole radiation due to distortion by crystalline fields

As already stated, the interatomic forces in solids create a non-vanishing transition probability  $\sigma_{III}$  even for forbidden lines if the crystalline fields make the wave functions lose their rigorous even-odd classification. A typical wave function for the ion in the crystal may be expressed as a linear combination

$$\psi = \psi_0^g + \Sigma_i a_i \psi_i^g + \Sigma_i b_i \psi_i^u \tag{12}$$

of the wave functions  $\psi_i$  of the free ion. The superscripts g and u denote respectively even and odd Laporte symmetry, and the sums are respectively over all the even and odd atomic states, which together yield a complete orthogonal set of wave functions. For simplicity, we have supposed that there are an even number of electrons, so that the original unperturbed wave function  $\psi_0$  for the given  $4f^x$  state is even. The order of magnitude of the amplitude q involved in expression 3 is

$$\int \psi' x \, \psi'' \, \mathrm{d}v = \Sigma_i \{ \int \psi_0^{g'} x \, b_i'' \psi_i^u \, \mathrm{d}v + \int b_i' \psi_i^u x \, \psi_0^{g''} \, \mathrm{d}v \}$$
  
 
$$\sim b_i \int \psi_i^g x \, \psi_i^u \, \mathrm{d}v \sim b_i r \quad (13)$$

Here we have made use of the fact that a matrix amplitude for an allowed transition connecting an even and odd state is comparable with the quantity r defined in expression 4. Perturbation theory shows that  $b_i = V_{\text{hem.}}/h\nu'$ , where  $V_{\text{hem.}}$  is a matrix element of the hemihedral part of the crystalline field, i.e., the portion which does not contain a center of symmetry. The formula for the transition probability becomes

$$\sigma_{\rm III} \sim (64\pi^4 e^2 \nu^3 r^2 / 3hc^3) (V_{\rm hem.} / h\nu')^2 \sim \sigma_{\rm allowed} (V_{\rm hem.} / h\nu')^2 \qquad (14)$$

Here  $\nu'$  must not be confused with  $\nu$ , and is the frequency interval separating  $4f^x$  from excited states of opposite Laporte symmetry. Its order of magnitude is  $\nu' \sim 10^5$  cm.<sup>-1</sup>

# IIIa. Naturally unsymmetrical fields

First let us consider fields which do not have a center of symmetry even at the equilibrium position. Such fields are doubtless somewhat smaller than the main portion of the crystalline field, so we take  $V_{\rm hem.} \sim 10 {\rm ~cm.^{-1}}$  Then expression 14 gives

$$\sigma_{\rm IIIa} \sim 1 \,\,\rm sec.^{-1} \tag{15}$$

## IIIb. Dissymmetry caused by vibration

In expression 1,  $x_i$ ,  $y_i$ ,  $z_i$  are the coördinates of the electron relative to an origin taken at the equilibrium position of the nucleus. Evidently if the nucleus vibrates, we have

$$x_i = x_i' + X, \quad y_i = y_i' + Y, \quad z_i = z_i' + Z$$
 (16)

where  $x_i', y_i', z_i'$  are the coördinates of the electron relative to the moving nucleus, and X, Y, Z are those of the nucleus relative to its equilibrium position. If the crystalline field has a center of symmetry, expression 1 will contain no odd powers of  $x_i, y_i, z_i$ , i.e., no terms of the form  $\mathbf{x}_i^s y_i^t z_i^u$ , where s + t + u is an odd integer. However, when the substitution (16) is made, odd powers of x', t', z' will appear. Then expression 1 becomes

$$V_{\text{crys.}} = \text{even terms in } x_i' y_i' z_i' + \Sigma_i \{ 2A_2 x_i' X + 2B_2 y_i' Y + \dots + 4A_4 x_i'^3 X + \dots \}$$
(17)

The breakdown of the Laporte selection rule is contingent upon the existence of odd powers of  $x_i'$ ,  $y_i'$ ,  $z_i'$  rather than of  $x_i$ ,  $y_i$ ,  $z_i$ , as the relevant symmetry is for the reflection in the nucleus as origin. The odd part of expression 17 is clearly of the order of magnitude R/r compared with the main, even crystalline potential, which we will denote by  $V_{\text{hol.}}$ . Here R

is the root mean square amplitude of nuclear vibration, and r is defined as in expression 4. So in expression 14 we now take

$$V_{\rm hem.} \sim (R/r) V_{\rm hol.}$$
 (18)

To estimate R, we use the relation

$$2\pi^2 \mu \omega^2 R^2 = \frac{1}{2} h v \omega \tag{19}$$

where  $\omega$  is the vibration frequency, v is the vibrational quantum number, and  $\mu$  is the effective reduced mass for the vibrating cluster (SmO<sub>6</sub>, PrO<sub>6</sub> etc.). Now  $\mu$  is comparable with the mass  $m_r$  of the rare-earth ion, so that we shall replace  $\mu$  by  $m_r$ . In fact,  $\mu$  would be identical with  $m_r$  if the oxygen atoms were rigidly connected to the rest of the crystal, so that they could not move. Actually, the connection is sufficiently stiff so that for local modes of vibration  $\mu$  is closer to  $m_r$  than, say, the mass of six oxygen atoms. If we take  $\omega \sim 100$  cm.<sup>-1</sup>,  $V_{hol.} \sim 100$  cm.<sup>-1</sup>, then by expressions 19, 18, and 14 we have  $R = \frac{1}{2} \times 10^{-9}$  cm., and

$$\sigma_{\rm HIb} \sim \frac{1}{10} \, \mathrm{sec.}^{-1} \tag{20}$$

## COMPARISON WITH EXPERIMENT

The transition probabilities observed by Becquerel and others in praseodymium and neodymium are of the order 10 to 100 sec.<sup>-1</sup> Our estimates of intensity due to any of the four causes I, II, IIIa, IIIb (equations 9, 11, 15, 20) all agree sufficiently with observation, as our calculations, admittedly rough, may easily be in error by a factor of 10 or 100. Much greater precision does not appear feasible at present, as it would require not only better knowledge of the wave functions of free rare-earth ions than now available, but also unknown exact information on the distortion of the outer orbits by the crystalline field. The one safe conclusion is that no one of the alternatives I, II, IIIa, IIIb can at present be ruled out on the basis of intensity, although IIIb does appear rather faint. Possibly lines exist due to all the causes; if so, one can readily see why the spectral phenomena observed by Spedding always present a more complicated front than do the magnetic data. More exact knowledge of crystalline forces can alone determine whether the hemihedry is really as important as assumed in IIIa. Decision between the various alternatives will probably be possible only when a detailed spectroscopic classification and Zeeman data become available for the various energy levels in the solid spectrum.<sup>3</sup> Then one can tell whether the effective selection rules and the Zeeman patterns are characteristic of quadrupole radiation, magnetic dipole

<sup>3</sup> Tentative attempts at classifying rare-earth spectra in solids have already been made by Tomaschek (Physik. Z. 33, 878 (1932)) and by Ellis (Phys. Rev. 49, 875 (1936)); the subject, however, seems to be still in an uncertain state.

radiation, or neither, and whether there is coupling to the vibrational structure of the type demanded by IIIb, which will be described more fully below. With the quadrupole hypothesis I, changes of more than two units in L or J are forbidden (also  $J = 0 \rightarrow J = 0, 1; L = 0 \rightarrow L = 0, 1$ ). With magnetic dipole radiation L or J cannot change by more than onunit (also  $J = 0 \rightarrow J = 0, L = 0 \rightarrow L = 0$  are absent). No such exclusions are found according to IIIa or IIIb. If the fourth-order terms in the potential (1) are the important ones, then changes of L or J are permitted up to and including 5 units<sup>4</sup> according to IIIa and 4 units according to IIIb.

# THE SPECIAL CASE OF GADOLINIUM, EUROPIUM, AND TERBIUM: INTERSYSTEM COMBINATIONS

In gadolinium, the ground state  $f^7 \, {}^8S$  is the only octet belonging to the configuration  $f^7$ . In europium and terbium, the ground level is the only septet of  $f^6$  or  $f^8$ . Hence the lines for these ions must be intersystem combinations as well as forbidden by the Laporte rule. They can hence exist only in virtue of spin-orbit interaction. The estimates (9, 15, 20) of intensity due to I, IIIa, IIIb must consequently all be reduced by a factor  $\alpha^2 \sim 1/100$ , and become respectively  $10^{-2}$ ,  $10^{-2}$ ,  $10^{-3}$  sec.<sup>-1</sup> For explanation of the factor  $\alpha$  see the discussion in connection with equation 10. No reduction is necessary in our estimate of 2 sec.<sup>-1</sup> for magnetic dipole radiation, as equation 11 already includes the factor  $\alpha^2$ . Magnetic dipole radiation thus appears somewhat more important than the other causes in gadolinium, europium, and terbium. Similar remarks apply to lines in any other rare earths that are intersystem combinations.

# THE MYSTERY OF THE EXTRA LEVELS

Many of the levels reported by Spedding (20) seem to fit rather well into the general scheme of the crystalline field. In some cases, however, there are states which cannot possibly be interpreted as Stark levels, for more levels would be required than could be obtained by a crystalline field of whatsoever symmetry. A notable example is samarium, where levels are found by Spedding (19) at 0, 160, 188, 225, and perhaps 245 cm.<sup>-1</sup>, although group theory shows that because of the inevitable Kramers (12) twofold degeneracy the  ${}^{6}H_{5/2}$  state characteristic of the normal Sm<sup>+++</sup> ion cannot possibly split into more than three levels under the influence of a crystalline field. Also levels are reported (18) at 0, 37, 53, 79 cm.<sup>-1</sup> for

<sup>&</sup>lt;sup>4</sup> Changes by five units are possible because a fourth-order field mingles states differing in L or J by up to four units, and this mixing effect is to be added to the unit changes permitted in ordinary free dipole radiation. With IIIb the permitted changes are one unit less, because only third-order terms in x', y', z' will appear in the odd part of 17, when expression 1 is of the fourth order in x, y, z.

 $GdCl_{3} \cdot 6H_{2}O$ , and at 0, 21, 41 cm.<sup>-1</sup> for  $Eu_{2}(SO_{4})_{3} \cdot 8H_{2}O$  (15), although an *S* state (<sup>8</sup>*S* ground state of  $Gd^{+++}$ ) doubtless does not split appreciably and a state with J = 0 (<sup>7</sup> $F_{0}$  ground state of  $Eu^{+++}$ ) manifestly can have only one component. There are three possible explanations of the extra levels.

1. They may be purely spurious, and due to some sort of a misclassification.

2. Some excited state may be depressed in energy so that it is comparable energetically with Stark components of the ground state. Following Spedding, we shall term such a potential deep-lying excited state an electronic isomer. In Sm<sup>+++</sup> the isomer would presumably be some multiplet component of  ${}^{6}H$  with  $J > \frac{5}{2}$ , and in Eu<sup>+++</sup> some component of  ${}^{7}F$  with J > 0.

3. The extra levels are somehow to be identified with vibration. By this we do not mean that any of the levels are purely vibrational, but rather that there is a certain interplay between vibrational and electronic motion, making the vibrational levels partake a little of the nature of crystalline Stark levels, and *vice versa*, so that the distinction between the two is lost. The agreement between observed and computed magnetic susceptibilities will not be destroyed, as one can show that both the specific heat and paramagnetic susceptibility are nearly the same as though the interplay were forgotten.

We shall not examine possibility 1, as it involves appraisals of spectroscopic technique and empirical analysis into energy levels which we do not feel competent to make. Also it seems to be belied by the consistency with which extra levels are reported. The alternative 2 is entirely incompatible with magnetic data,<sup>5</sup> as well as with recent work on the spectra of free rare-earth ions. Recent spectroscopic measurements by Albertson (2) on configurations of Sm, Sm<sup>+</sup> which differ from Eu<sup>+++</sup> only by addition of one or two unimportant 6s electrons, show that the multiplet intervals assumed by Miss Frank in her magnetic calculations (9) on Eu<sup>+++</sup>, which were made before the spectroscopic data were available, are substantially correct.<sup>6</sup> Analogous information is not yet available for Sm<sup>++++</sup>, but analogy to Eu<sup>+++</sup> leaves but little doubt that the multiplet intervals assumed by Miss Frank in Sm<sup>++++</sup> are also reasonable, and that there is no low-lying electronic isomer.

We must, however, mention that specific heat data, if we can rely on them literally, would seem to indicate that the extra levels are due to some kind of electronic isomer rather than to vibration. Ahlberg and Freed (1) have assumed that vibrational effects cancel out in comparing the specific heats of gadolinium and semarium salts, so that their difference records

<sup>&</sup>lt;sup>5</sup> For a general discussion of the magnetism of the rare-earth group see Chap. IX of reference 24, also references 16 and 9.

<sup>&</sup>lt;sup>6</sup> This point will be discussed more fully in a future paper by Miss Frank.

the purely electronic contribution. The measured difference agrees better with the assumption of four than three crystalline levels, whereas we have seen that not more than three are permitted unless an electronic isomer is introduced. However, the agreement with three levels is fair,<sup>7</sup> and the differential specific heat is hard to measure accurately, as it is very small relative to that of either gadolinium or samarium. For instance,  $C_p$  is 60 cal. per mole at 100°K. for  $Gd_2(SO_4)_3 \cdot 8H_2O$ , and 62.2 for  $Sm_2(SO_4)_3 \cdot 8H_2O$ , whereas the difference is only 2.2. Quite apart from possible experimental error, it is conceivable that the vibration frequencies of the two salts may be slightly unlike, more than one would conjecture from the mere mass difference in the cation. The perturbation effect discussed in fine print below gives rise to precisely this situation. So it seems dangerous to draw definite conclusions from specific-heat data at the present time.

Our preference is for possibility 3, in which coupling between vibration and electronic motion is hypothecated. It will be realized if our effect IIIb is the proper explanation of the intensity of some of the lines. Namely, if we use I, II, or IIIa to account for the intensity, the strong lines are those in which the vibrational quantum number is unaltered. With IIIb it is easily seen (see below) that the most probable transitions are those in which the vibrational quantum number v changes by one unit. The observed frequencies are then not  $\nu_0$ , but rather  $\nu_0 \pm \omega$ , where  $\omega$  is the vibrational frequency, and  $\nu_0$  is the frequency which would be obtained were the vibrational part of the energy neglected. In this event, the electronic energy levels cannot be obtained correctly without allowing for the vibrational modulation, and when allowance is not made for this fact, vibrational levels may be misinterpreted as crystalline levels. We do not believe that IIIb is the main cause of intensity, but it is quite possible that some radiation of this type is mixed in with the others, just enough to cause confusion and give the apparent extra levels.

To prove that in IIIb the effective frequencies are  $\nu_0 \pm \omega$  rather than  $\nu_0$ , we note that in equation 17 the terms which are odd in x, y, z and which are needed to break down the Laporte rule are linear in the vibrational coördinates X, Y, Z. (Higher powers of X, Y, Z would be smaller and hence less important.) The non-vanishing matrix elements of X, Y, Z involve changes of one unit in the appropriate vibrational quantum number (which is in general different for X, Y, and Z). Hence the significant part of equation 17 couples together states differing by one unit in v. Consequently the odd part of equation 12 is composed of terms differing by one unit in v, a non-vanishing value of the transition amplitude 13 is obtained only if the odd part of  $\psi'$  contains terms of the same vibra-

<sup>7</sup> Cf. figure 4 of Miss Frank's second paper (9).

tional quantum number as the main part of  $\psi''$ , or vice versa. Hence  $\psi_0'$ must differ by one unit in  $v \operatorname{from} \psi_0''$ . The situation may be likened in some ways to that in radiation theory. Just as in the latter the coupling of the electronic motion to the ether causes electron transitions to be accompanied by changes of one quantum unit in the radiation harmonic oscillators, so in our theory the vibration-rotation coupling causes transitions to be accompanied by changes of one unit in the vibrational quantum number.

There may also be the following effect, which may be regarded as a variant of IIIb. It is well known that in the band spectrum of carbon dioxide, there is a resonance effect (7,8), whereby two close-lying levels share their properties with each other, owing to perturbing matrix elements connecting them. In consequence the two states, so to speak, lose their identity. In this way, both of them are able to combine with other states by means of the same selection rules and be manifested in the Raman effect, whereas without the perturbation, only one of the two levels would be detectable. Similarly in our case it may happen that a vibrational level (for example, a level in which one quantum of vibration is excited) happens to fall very near a crystalline Stark level in which no vibration. If there is appreciable perturbation coupling connecting the two levels, then obviously they can make the same combinations with other states. In this way the number of apparent crystalline Stark levels is doubled as far as spectroscopic observation is concerned.

We are thus led to investigate when there can be appreciable matrix elements connecting a vibrational and a Stark state. The requisite perturbing potential must be linear in the vibrational coördinates, as higher powers are too small to be important. The connected levels then differ by one unit in some vibrational quantum number. The perturbing potential must be even in  $x'_i$ ,  $y'_i$ ,  $z'_i$ , as two different Stark components of the same electronic level have the same Laporte parity. It thus might seem that only a hemihedral crystalline potential could be effective, as odd powers of  $x_i, y_i, z_i$  give rise to even powers of  $x'_i, y'_i, z'_i$  and vice versa, when one makes the substitution  $x = x'_i + X$ , etc., and retains only linear terms in X, Y, Z. If  $V_{\rm hem} \sim 10~{\rm cm}$ .<sup>-1</sup>, the matrix elements thus arising are of the order  $V_{\rm hem}$ . $(R/r) \sim$ 0.3 cm.<sup>-1</sup>, and hence too small to be important. This conclusion, however, is on the basis of a "one-atom treatment," wherein only the paramagnetic ion vibrates. If instead the whole cluster (e.g.,  $SmO_6$ ) is included as a dynamical unit, it can be shown that certain modes of vibration give rise to even terms in  $x'_i$ ,  $y'_i$ ,  $z'_i$  regardless of whether the potential has a center of symmetry. Our considerations on this subject, to be amplified elsewhere, are closely related to those which were presented in a rather different connection and terminology by Jahn and Teller at the April, 1936, meeting of the American Physical Society. In consequence there can be matrix elements of the order  $V_{\rm hol}$ .  $(R/r) \sim 3$  cm.<sup>-1</sup> Levels separated by such an amount will lose all their identity, and those separated by ten times this amount will become sufficiently mixed so that combinations permitted for one level will also be allowed for the other with an intensity about 1/100 as great.

#### DIGRESSION ON THE IRON GROUP

Our discussion has been intended primarily for the rare earths, but can easily be adapted to the study of the sharp lines emitted by chromic salts and other salts of the iron group in the solid state. The main difference is that the crystalline potential is about one hundred times larger, and so the estimate 20 of the transition probability IIIb must be increased by a factor 10<sup>4</sup>. There are no great changes in the estimates 9 and 11 for quadrupole and magnetic dipole radiation. The careful x-ray analysis of Lipson and Beevers (14) shows that in chrome potassium alum, the field surrounding the chromic ion has a center of symmetry, so that here hypothesis IIIa must be discarded. Because of the large crystalline field, the resonance effect discussed above is adequate to merge two levels separated by 300  $cm.^{-1}$  or so. Perhaps this fact may explain the apparent electronic isomer reported by Spedding and Nutting (22) in chrome alum at 38 cm.<sup>-1</sup>, which is quite incomprehensible if taken literally, since magnetic data show conclusively that only one electron state is inhabited. The interaction between electronic and vibrational motion seems to furnish a clue to the understanding of the interesting Zeeman measurements (22) of these authors and of the magnetic behavior of vanadium and titanium salts, as I shall discuss elsewhere.

#### CONCLUSION

The sharp lines in the rare earths are forbidden lines violating the Laporte rule. They probably do not originate in any one cause, but are rather to be attributed to a variety of effects, viz., quadrupole radiation, magnetic dipole radiation, and radiation created by crystalline fields in which the requisite departures from a center of symmetry are either present at the equilibrium position or caused by atomic vibrations. It appears likely that there is some interplay between vibration and electronic motion, as otherwise it is very hard to understand the extra levels reported by Spedding.

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