Crystal-field analysis for the susceptibility of lanthanide compounds of the form Cs_2NaRCl_6[†]

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We have used crystal-field theory to discuss susceptibility data for the compounds Cs_2NaRCl_6 where R = Ce, Nd, Tb, Dy, Ho, Tm, and Yb. These materials have an octahedral coordination for the lanthanide ion which remains undistorted even at low temperatures. A combined analysis of all the susceptibility data provides the crystal-field interaction parameters $A_4\langle r^4 \rangle = 254 \langle r^4 \rangle$ K and $A_6 \langle r^6 \rangle = 4 \langle r^6 \rangle$ K with $\langle r^4 \rangle$ and $\langle r^6 \rangle$ in atomic units. The numerical values A_4 and A_6 are independent of the lanthanide ion within experimental error. Attempts to explain these results within a simple point-charge model were unsuccessful.

I. INTRODUCTION

In considering systems which may be useful for simple studies of crystal-field effects, a number of criteria seem important: (i) the material should be cubic so that the number of crystal-field parameters is minimized; (ii) the material should be magnetically dilute so that the electronic properties can be measured over a wide range of temperatures without having the complication of magnetic exchange interactions introduced; (iii) in order to discuss the crystal-field parameters obtained from the simplest points of view, it is desirable that the material be nonmetallic, and as ionic as possible. These conditions have been partially met in the past by a number of materials which have octahedral coordination of the metal ion with halide ions in the first-neighbor shell. However, almost all such lanthanide compounds distort at low temperatures, demanding that numerous crystal-field parameters be determined. At present, the only known exceptions are for those compounds which have the "ideal cryolite" structure. In this paper, we wish to consider crystal-field interactions for one class of these compounds having the general form Cs_2NaRCl_6, where R is a trivalent lanthanide ion.[1-3] The crystal structure for these compounds is shown in Fig. 1. The first-neighbor coordination for the lanthanide ion is an octahedron of chlorine ions, the second-shell coordination is a simple cube of Cs ions, the third-shell coordination is an octahedron of Na ions, etc. The R ions appear again only in the fifth-neighbor shell. Furthermore, a number of measurements on some of those compounds show that the cubic coordination remains even at low temperatures.[4-6]

Compounds of this kind would thus appear to be very good model systems for the study of crystal-field interactions. Furthermore, since the compounds can be made from all R ions spanning the entire series, one is able to consider variations of the crystal-field model across the series and make comparison with theoretical predictions. Magnetic susceptibility measurements have been recently reported for the closely related materials Rb_2NaRF_6; however, in that case the emphasis was placed on the very-low-temperature data and on the low-lying crystal-field states only.[7] Susceptibility data for the Cs_2NaRCl_6 cryolites have been previously reported, and a preliminary analysis of these data given.[8,9] Here we present a more complete discussion of these data within the framework of simple crystal-field theory. We have analyzed the detailed temperature dependence of the susceptibility for those compounds with R = Ce, Nd, Tb, Dy, Ho, Tm, and Yb. Specific results for each of these will be discussed, crystal-field parameters derived for the entire series, and comparison to elementary point-charge calculations will be made.

II. ANALYSIS AND RESULTS

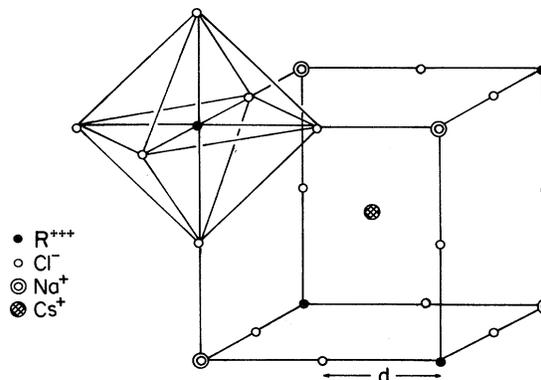The theoretical formalism required for the analysis of the susceptibility data is well establish-

FIG. 1. Crystal structure for the compounds Cs_2NaRCl_6.

ed and needs only a few summarizing statements, largely for the purpose of establishing notation. We use the description of Van Vleck[10] and consider a angular momentum manifold J with a

gyromagnetic ratio of g_J. Owing to whatever interactions may be present, this state is split into a series of states $|n\rangle$ at energies E_n, where $n = 1$ to $2J + 1$. The susceptibility is then given by

$$\chi = \frac{N_0 g_J^2 \mu_B^2}{kT} \frac{\sum_n [\, |\langle n|J_z|n\rangle|^2 - 2\sum_{n'} |\langle n|J_z|n'\rangle|^2 \, kT/(E_n - E_{n'})] e^{-E_n/kT}}{\sum_n e^{-E_n/kT}} . \tag{1}$$

In this expression, the first term under the summation represents the direct contribution of the level n to the susceptibility, while the second term gives the "induced" or "Van Vleck" susceptibility which arises from admixtures of all the levels n' into n when an external field is applied during the susceptibility measurement.

In the case of interest here, the n levels are determined solely by the crystal-field interaction. The problem of rare-earth ions in cubic symmetry has been extensively discussed by Lea, Leask, and Wolf (LLW).[11] In cubic symmetry, two terms are sufficient to specify the crystal-field potential. The Hamiltonian for this case can be written

$$\mathcal{H}_{CF} = B_4(O_4^0 + 5O_4^4) + B_6(O_6^0 - 21O_6^4), \tag{2}$$

where the factors O_m^n are Stevens operators acting on the J angular momentum states, and the two quantities B_m are numerical factors which depend on the electronic charge distribution in the crystal being considered. These are frequently related to parameters A_m by

$$B_4 = A_4 \langle r^4 \rangle \, \beta,$$
$$B_6 = A_6 \langle r^6 \rangle \, \gamma, \tag{3}$$

where $\langle r^4 \rangle$ and $\langle r^6 \rangle$ are radial averages over the $4f$ electrons of the ion in question, while β and γ are Stevens multiplicative factors. The radial parameters $\langle r^n \rangle$ in turn are often related to calculated free-ion Hartree-Fock values $\langle r^n \rangle_{HF}$ through a shielding constant σ_n such that $\langle r^n \rangle = (1 - \sigma_n)\langle r^n \rangle_{HF}$. In addition, LLW define parameters W and x such that x varies from -1 to $+1$ as the ratio B_4/B_6 covers all possible values. All of these quantities are interrelated as follows:

$$Wx = B_4 F(4) = A_4 \beta \langle r^4 \rangle F(4)$$
$$= A_4 \beta (1 - \sigma_4)\langle r^4 \rangle_{HF} F(4),$$
$$W(1 - |x|) = B_6 F(6) = A_6 \gamma \langle r^6 \rangle F(6)$$
$$= A_6 \gamma (1 - \sigma_6)\langle r^6 \rangle_{HF} F(6), \tag{4}$$

where again $F(4)$ and $F(6)$ are numerical factors. For convenience we present in Table I all of these

TABLE I. Numerical constants useful for crystal-field calculations with rare-earth ions. Values are taken from Ref. 11 except for the radial parameters $\langle r^4 \rangle_{HF}$ and $\langle r^6 \rangle_{HF}$ which are from Ref. 13.

Ion and configuration	g_J	$10^{-4}\beta$	$F(4)$	$\langle r^4 \rangle_{HF}$ [a]	$\beta F(4)\langle r^4 \rangle_{HF}$	$10^{-6}\gamma$	$F(6)$	$\langle r^6 \rangle_{HF}$ [b]	$\gamma F(6)\langle r^6 \rangle_{HF}$
Ce^{3+} $^2F_{5/2}$	$\frac{6}{7}$	63.492	60	3.455	1.316 19	0	$\cdots$	21.226	0
Pr^{3+} $^3H_4$	$\frac{4}{5}$	-7.3462	60	2.822	-0.124 39	60.994	1260	15.726	1.208 58
Nd^{3+} $^4I_{9/2}$	$\frac{8}{11}$	-2.9111	60	2.401	-0.041 94	-37.988	2520	12.396	-1.186 67
Sm^{3+} $^6H_{5/2}$	$\frac{2}{7}$	25.012	60	1.897	0.284 69	0	$\cdots$	8.775	0
Tb^{3+} $^7F_6$	$\frac{3}{2}$	1.2244	60	1.419	0.010 42	-1.1212	7560	5.688	-0.048 21
Dy^{3+} $^6H_{15/2}$	$\frac{4}{3}$	-0.5920	60	1.322	-0.004 70	1.0350	13 860	5.102	0.073 19
Ho^{3+} $^5I_8$	$\frac{5}{4}$	-0.3330	60	1.219	-0.002 44	-1.2937	13 860	4.502	-0.080 72
Er^{3+} $^4I_{15/2}$	$\frac{6}{5}$	0.4440	60	1.126	0.003 00	2.0699	13 860	3.978	0.114 12
Tm^{3+} $^3H_6$	$\frac{7}{6}$	1.6325	60	1.067	0.010 45	-5.6061	7560	3.647	-0.154 57
Yb^{4+} $^2F_{7/2}$	$\frac{8}{7}$	-17.316	60	0.960	-0.099 74	148.00	1260	3.104	0.578 83

[a] In units of a_0^4 where a_0 is the Bohr radius.
[b] In units of a_0^6.

numerical constants for the rare-earth ions, except for the shielding factors σ_n. No experimental values for these quantities exist. However, theoretical calculations[12] give values of $\sigma_4 \approx 0.1$ and $\sigma_6 \approx 0.04$ for trivalent ions in the lanthanide series. In view of other uncertainties in the following analysis, these rather small corrections will not be a major consideration. We will therefore presume in the following that $\langle r^n \rangle = \langle r^n \rangle_{HF}$ for $n = 4$ and 6. For completeness, however, it should be noted that this identification is not correct in cases where second-order ($n = 2$) terms are important, since the corresponding shielding factor has a value $\sigma_2 \approx 0.5$.[12]

Wave functions and energies for the crystal-field levels of the rare-earth ions in cubic symmetry are given by LLW. From these one can apply Eq. (1) and calculate the susceptibility directly. In a few cases, the state is split into only two or three levels, and the wave functions in some cases are independent of the specific values of B_4 or B_6. It is then possible to obtain a convenient closed-form expression for the susceptibility. In most other cases, however, closed-form expressions become cumbersome and can be written simply only for low-temperature limits. In many cases, therefore, we have used a direct numerical calculation of the susceptibility. The Hamiltonian, consisting of the crystal-field potential plus the electronic Zeeman interaction from the applied field, was diagonalized to yield energy values and wave functions. From these, the thermal average of the magnetization $\langle M_z \rangle$ was determined and the susceptibility obtained as $\langle M_z \rangle /H$, where H is the applied field. Since such a procedure treats the Zeeman interaction and the crystal field on an equal basis, the Van Vleck induced contributions to the susceptibility are automatically included. The results obtained were checked for a variety of values of H in order to be sure that a proper low-field limit was obtained. In those cases where closed-form expressions could be easily obtained from Eq. (1), agreement with the numerically determined susceptibility was excellent. This routine was then coupled to a least-squares fitting program, and a search was made to determine the best values of W and x [see Eq. (4)] for each compound. In the following, we present results for several of the compounds, along with a discussion of some aspects of the effects of the cubic crystal field on the susceptibility in general.

A. $Cs_2NaCeCl_6$

In the presence of an octahedral field, the $^2F_{5/2}$ state of Ce^{3+} is split into a low-lying Kramer's

doublet (Γ_7) and an excited quartet (Γ_8). The susceptibility for this case can be calculated exactly to be[14,15]

$$\chi = \frac{g_J^2 \mu_B^2 J(J+1)}{3kT}$$

$$\times \left[\frac{5 + 26e^{-\Delta_{78}/kT} + 32(kT/\Delta_{78})(1 - e^{-\Delta_{78}/kT})}{21(1 + 2e^{-\Delta_{78}/kT})} \right], (5)$$

where $\Delta_{78} = E_8 - E_7$ is the $\Gamma_7 - \Gamma_8$ separation. Here, the first term in the bracket is the direct contribution from Γ_7, the second term that from Γ_8, and the third term is the induced contribution arising from $\Gamma_7 - \Gamma_8$ mixing. In Fig. 2(a), the inverse susceptibility given by this expression is plotted as a function of kT/Δ_{78}. Also shown are the limiting-Curie-law susceptibilities appropriate to the isolated Γ_7, the isolated Γ_8, and the free ion. Characteristically, one sees an increase in $1/\chi$ due to the crystal-field effects at low temperatures, with the susceptibility returning to the free-
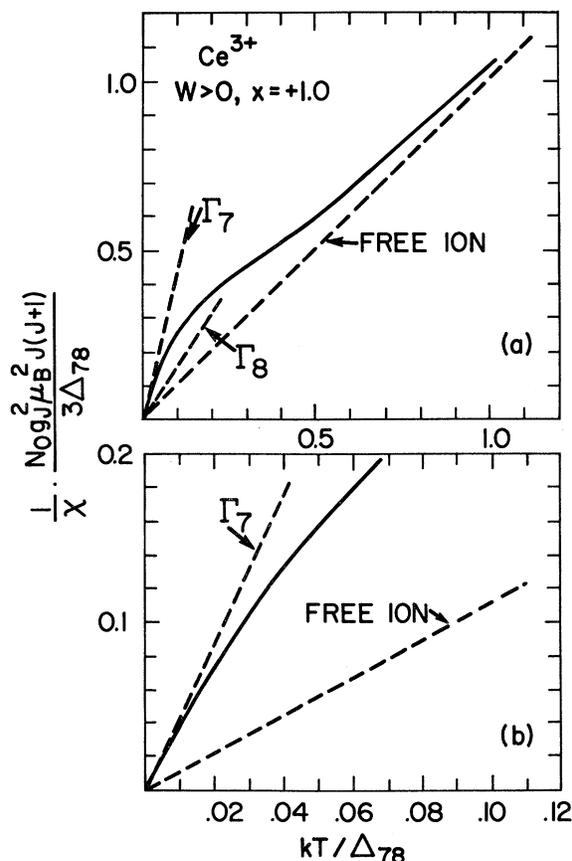

FIG. 2. Crystal-field effects on the susceptibility of Ce^{3+} in octahedral symmetry. The energy difference between the ground state Γ_7 and the excited state Γ_8 is given by Δ_{78}.

ion value and slope at $kT \approx \Delta_{78}$. Figure 2(b) shows an expanded view of the low-temperature region. As $T \to 0$, the susceptibility approaches the Γ_7 value, as it must. However, the induced susceptibility between Γ_7 and Γ_8 is quite large, even at rather low temperatures. As a result, the observed susceptibility deviates from the Γ_7 limit for $kT \approx 0.01\Delta_{78}$, even though the Γ_8 Boltzmann factor is still negligible at this temperature.

The measured susceptibility for $Cs_2NaCeCl_6$ is shown in Fig. 3. For a $J = \frac{5}{2}$ level one has $x = +1$, which is to say that sixth-order terms in the crystal-field potential play no role. As a result, the data are described by a single crystal-field parameter. For $W = 334$ K (corresponding to Δ_{78} $= 2000$ K), obtained by a least-squares fit of Eq. (1) to the measured susceptibility, the solid line is obtained.[16]

It should be noted that in this case the crystal-field splitting is of comparable magnitude with the spin-orbit splitting[6] between the $^2F_{5/2}$ and $^2F_{7/2}$ levels of the Ce^{3+} ion. Thus physical parameters should properly be calculated including admixture of the $^2F_{7/2}$ state into the ground state. We have not done so in detail for this case, but some preliminary calculations indicate that inclusion of the spin-orbit energy changes the calculated susceptibility by about 10%

B. $Cs_2NaNdCl_6$

The cubic crystal field splits the $^4I_{9/2}$ state of Nd^{3+} into a doublet (Γ_6) and two quartets ($\Gamma_8^{(1)}$ and $\Gamma_8^{(2)}$). In an octahedral environment, the ground state is expected to be either Γ_6 or $\Gamma_8^{(2)}$, depending on the prevalent value of x. From the low-temperature susceptibility data shown in Fig. 4, one identifies $\Gamma_8^{(2)}$ as the ground state. The solid line
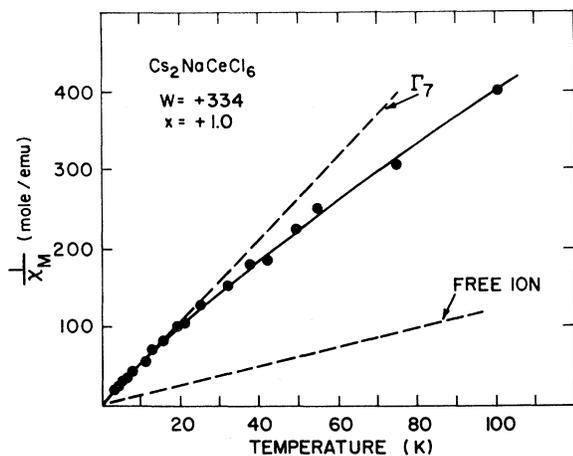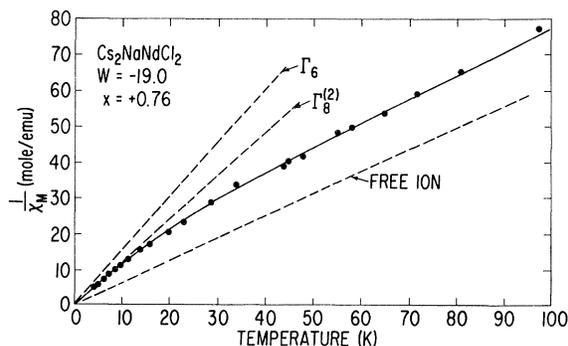

FIG. 4. Measured and calculated susceptibility for $Cs_2NaNdCl_6$.

is a fit to the data for the indicated parameters, which give Γ_6 as the first excited state at 290 K above the ground state, with $\Gamma_8^{(1)}$ lying at 930 K. This is not in good agreement with values estimated from optical measurements[17]; however, in this case the susceptibility probably provides a more reliable measure of the crystal field.

C. $Cs_2NaTbCl_6$

In a cubic field, the $^7F_6$ state of Tb^{3+} is split into two singlets (Γ_1 and Γ_2), one nonmagnetic doublet (Γ_3) and three triplets [Γ_4, $\Gamma_5^{(1)}$, and $\Gamma_5^{(2)}$]. For octahedral coordination, the ground state should be either Γ_1 or Γ_2. A nonmagnetic ground state is clearly seen by the leveling of $1/\chi$ vs T at low temperatures, shown in the data of Fig. 5. For the likely case $x \lesssim -0.5$, the ground state will be Γ_1, with the higher-state ordering being Γ_4, $\Gamma_5^{(2)}$, Γ_2, $\Gamma_5^{(1)}$, and Γ_3. Inspection of the wave functions shows that an induced susceptibility at very low temperatures will occur by interaction
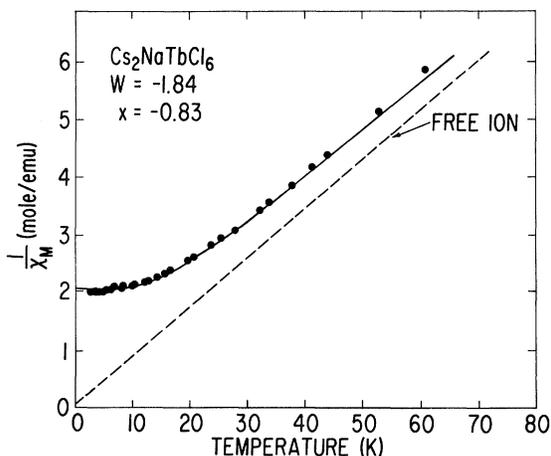

FIG. 3. Measured and calculated susceptibility for $Cs_2NaCeCl_6$.

FIG. 5. Measured and calculated susceptibility for $Cs_2NaTbCl_6$.

between the ground state Γ_1 and the two levels Γ_3 and Γ_4. Evaluating Eq. (1) for this case at $T = 0$ gives

$$\chi(0) = N_0 g_J^2 \mu_B^2 \left(\frac{7}{2\Delta_{13}} + \frac{28}{\Delta_{14}} \right), \qquad (6)$$

where $\Delta_{13} = E_3 - E_1$ is the $\Gamma_1 - \Gamma_3$ splitting, and $\Delta_{14} = E_4 - E_1$ is the $\Gamma_1 - \Gamma_4$ splitting. From the LLW diagrams we may estimate $\Delta_{13} \sim 10\Delta_{14}$. If we therefore consider the first contribution to be small, and take $g_J = \frac{3}{2}$, Eq. (6) becomes

$$\chi(0) = 189/8\Delta_{14} \text{ emu/mole} \qquad (7)$$

with Δ_{14} in degrees K.

For $Cs_2NaTbCl_6$, the value $\chi(0) = 0.50$ emu/mole gives $\Delta_{14} = 47$ K. The solid line in the figure is a computer fit yielding the values of W and x indicated. The over-all crystal-field splitting is found to be $\Delta_{13} = 414$ K.

D. Cs₂NaDyCl₆

The cubic crystal field splits the $^6H_{15/2}$ state of Dy^{3+} into two Kramer's doublets (Γ_6 and Γ_7) and three quartets ($\Gamma_8^{(1)}$, $\Gamma_8^{(2)}$, and $\Gamma_8^{(3)}$). In octahedral coordination with $-1.0 \leqslant x \leqslant -0.45$, one anticipates a Γ_6 ground state with the higher states following the ordering $\Gamma_8^{(1)}$, Γ_7, $\Gamma_8^{(2)}$, and $\Gamma_8^{(3)}$. For Dy cases, the over-all crystal-field splitting is rather small, and very low temperatures are necessary to verify the ground state directly from the susceptibility measurements. However, the detailed least-squares fit to the $Cs_2NaDyCl_6$ data (Fig. 6) is in agreement with this ordering. For the parameters given in the figure, one obtains a $\Gamma_8^{(1)} - \Gamma_6$ separation of 34 K and an over-all splitting ($\Gamma_8^{(3)} - \Gamma_6$) of 350 K.

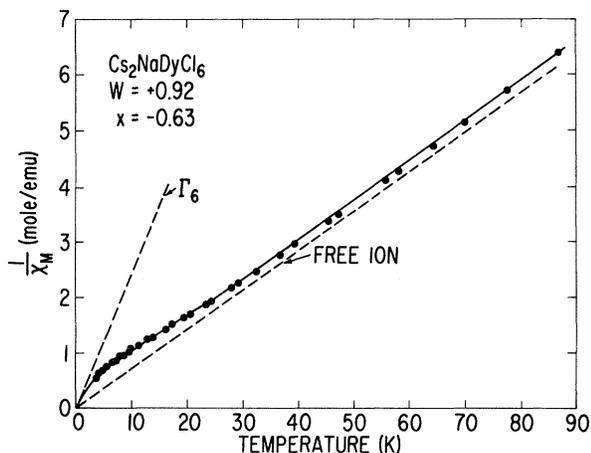### E. Cs₂NaHoCl₆

In a cubic field, the $^5I_8$ state of Ho^{3+} splits into one singlet (Γ_1), two nonmagnetic doublets [$\Gamma_3^{(1)}$ and $\Gamma_3^{(2)}$], and four triplets [$\Gamma_4^{(1)}$, $\Gamma_4^{(2)}$, $\Gamma_5^{(1)}$, and $\Gamma_5^{(2)}$]. The ground state for octahedral coordination should be either Γ_1 or $\Gamma_3^{(2)}$. However, the LLW diagram is complicated, with a great deal of level crossing occurring, which make simple predictions difficult. The complete analysis of the $Cs_2NaHoCl_6$ data (see Fig. 7) gives a $\Gamma_3^{(2)}$ ground state. For the parameters shown, the level ordering is $\Gamma_3^{(2)}$, $\Gamma_4^{(2)}$, $\Gamma_1, \Gamma_4^{(1)}$, $\Gamma_5^{(2)}$, $\Gamma_3^{(1)}$, and $\Gamma_5^{(1)}$ with the splitting $\Gamma_4^{(3)} - \Gamma_4^{(2)}$ being only 11 K and the over-all splitting $\Gamma_5^{(1)} - \Gamma_3^{(2)}$ being 577 K.

F. Cs₂NaTmCl₆

The $^3H_6$ level of Tm^{3+} is split by the cubic crystal field in a manner identical to that of Tb^{3+}, which also has $J = 6$. Again, one anticipates a Γ_1 ground state with Γ_4 being the first excited state and Γ_3 the highest level. From Eq. (6) one obtains a zero-field susceptibility due to interaction between Γ_1 and Γ_4,

$$\chi(0) = \tfrac{343}{24} \Delta_{14} \text{ emu/mole}, \qquad (8)$$

where we have used $g_J = \tfrac{7}{6}$, and where Δ_{14} is in units of degrees K. From the data of $Cs_2NaTmCl_6$ (see Fig. 8), we obtain $\chi(0) = 0.2$ emu/mole, which gives $\Delta_{14} = 71$ K. The complete temperature dependence gives the W and x values indicated in the figure, from which one obtains an overall crystal-field splitting $\Gamma_3 - \Gamma_1$ of 638 K.

G. Cs₂NaYbCl₆

The $^2F_{7/2}$ state of Yb^{3+} is split by the cubic field potential into two doublets (Γ_6 and Γ_7) and one

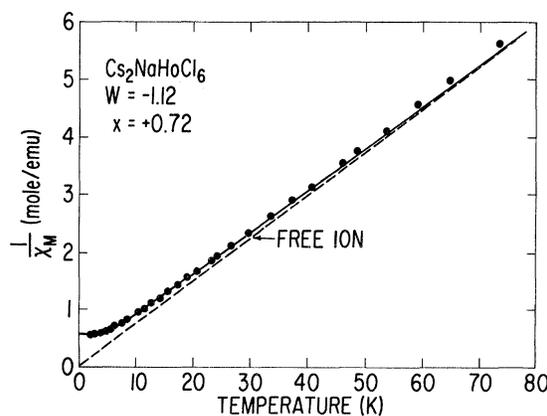FIG. 6. Measured and calculated susceptibility for $Cs_2NaDyCl_6$.

FIG. 7. Measured and calculated susceptibility for $Cs_2NaHoCl_6$.

quartet (Γ_8). For octahedral symmetry with $x \leq -0.6$, one expects the Γ_6 state to be lowest with Γ_8 next and Γ_7 highest. For the $J = \frac{7}{2}$ case, the wave functions are independent of x; so a closed-form expression for χ may be conveniently obtained. From Eq. (1) and the LLW wave func-

tions, this is found to be

$$\chi = \frac{g_J^2 \mu_B^2 J(J+1)}{3kT} f(T), \tag{9}$$

where

$$f(T) = \left(98 + 260 e^{-\Delta_{68}/kT} + 162 e^{-\Delta_{67}/kT} + \frac{432 kT}{\Delta_{68} - \Delta_{67}} \left(e^{-\Delta_{67}/kT} - e^{-\Delta_{68}/kT} \right) \right.$$
$$\left. + \frac{560 kT}{\Delta_{68}} \left(1 - e^{-\Delta_{68}/kT} \right) \right) \Big/ 378 \left(1 + 2 e^{-\Delta_{68}/kT} + e^{-\Delta_{67}/kT} \right). \tag{10}$$

Here $\Delta_{68} = E_8 - E_6$ is the energy difference between the Γ_6 and Γ_8 levels, and $\Delta_{67} = E_7 - E_6$ is that between Γ_7 and Γ_6. The first three terms in $f(T)$ are the direct contributions from Γ_6, Γ_8, and Γ_7, respectively. The fourth term is due to $\Gamma_7 - \Gamma_8$ mixing and the fifth due to $\Gamma_6 - \Gamma_8$ mixing. No mixing occurs between Γ_6 and Γ_7. In Fig. 9 we show the low-temperature-limiting form, where χ is plotted as a function of kT/Δ_{68} for temperatures such that $\Delta_{67} \gg kT$. The appropriate Curie-law susceptibilities for the free ion and for the isolated Γ_6 level are also shown. Here one sees again the strong role played by the induced susceptibility. Deviations occur from the Γ_6 values for temperatures as low as $kT \approx 0.03 \Delta_{68}$. At these temperatures, the Γ_8 level is not substantially populated, but the Van Vleck term arising from mixing between Γ_6 and Γ_8 is quite substantial. This was also noted previously for the compound Rb_2NaYbF_6.[18]

The measured susceptibility for $Cs_2NaYbCl_6$ is shown in Fig. 10. For the values of W and x indicated, the ground state is Γ_6, with Γ_8 at 390 K and Γ_7 at 830 K.[16]
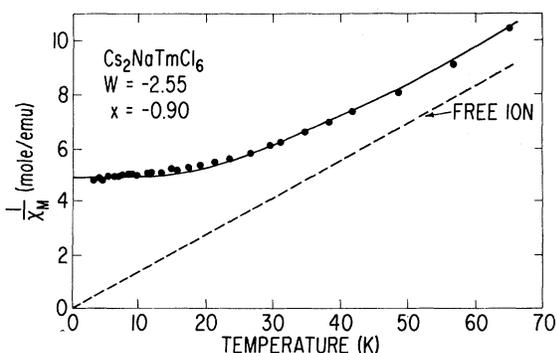
III. DISCUSSION

In Table II we summarize the crystal-field parameters obtained from the analysis of the susceptibility data for these compounds. In Fig. 11, the quantities Wx and $W(1 - |x|)$ are plotted against $\beta F(4)\langle r^4 \rangle$ and $\gamma F(6)\langle r^6 \rangle$, respectively, [see Eq. (4)]. The solid line is drawn on the assumption that A_4 and A_6 are constants throughout the series. One sees that this simple assumption is rather well satisfied for both parameters, the only exceptions being with the Wx values for the Dy and Tb compounds. Whether these differences are significant cannot be decided at present. A least-squares fit of a straight line to the data gives
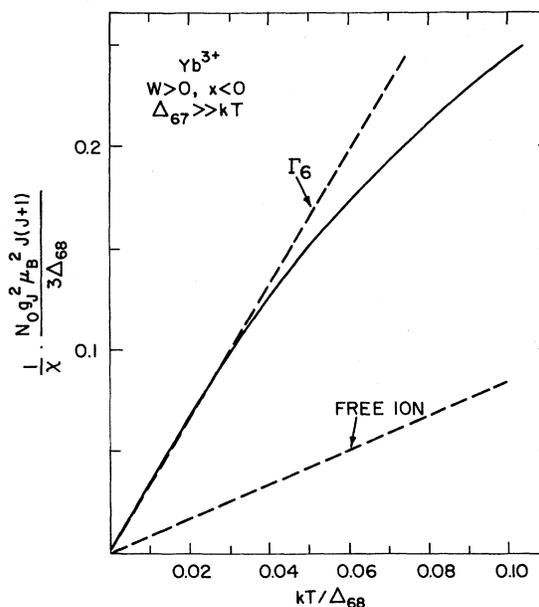

FIG. 8. Measured and calculated susceptibility for $Cs_2NaTmCl_6$.

FIG. 9. Low-temperature susceptibility for Yb^{3+} in octahedral symmetry. The energy difference between the ground state Γ_6 and the first excited state Γ_8 is Δ_{68}.

$$A_4 = 254a_0^{-4} \text{ K}, \quad A_6 = 4a_0^{-6} \text{ K}, \tag{11}$$

where a_0 is the Bohr radius. Note that with $\langle r^4 \rangle$ and $\langle r^6 \rangle$ in atomic units as in Table I, the quantities B_4 and B_6 [see Eq. (3)] are obtained directly from this in units of degrees K.

The result of an essentially constant A_4 and A_6 has been previously used as a first-order approximation in extrapolating or interpolating crystal-field data for rare-earth compounds; however, no reliable test of the assumption has been previously available. Data are available from optical spectroscopy for a number of lanthanides present as impurities in $LaCl_3$ and for several of the lanthanide ethylsulfates.[19] In those cases the evidence seems to favor constant values of the B_n (rather than A_n) across the series. However, there is a great deal of scatter in the data and a clear conclusion does not seem possible. The clearest previous case concerns optical work on the $LaCl_3 \cdot 6H_2O$ compounds. Harrop[20] has discussed a large amount of such data and has shown that an assumption of constant A_n can be used very effectively there. Nonetheless all the previous work is complicated by the fact that the symmetry is at best hexagonal, and in the $RCl_3 \cdot 6H_2O$ case only a two fold symmetry axis exists. Thus the cubic symmetry in the present case, with the commensurate simplification of the crystal-field Hamiltonian, provides a situation considerably easier to treat than has been previously available.

We may attempt to interpret the A_4 and A_6 values obtained above on the basis of a simple point-charge model, since the crystal structure is well known and the ionic charges are easily assigned. In such a calculation, the principal uncertainty is the position d of the Cl^- ion relative to the central R^{3+} ion (see Fig. 1). Careful x-ray studies[2] have shown that for Cs_2NaErF_6, this distance is $d = 0.26a$, where a is the lattice constant. In order to make an estimate of the crystal fields, we will take $d = 0.25a$, i.e., we take the Cl^- ion to be situ-
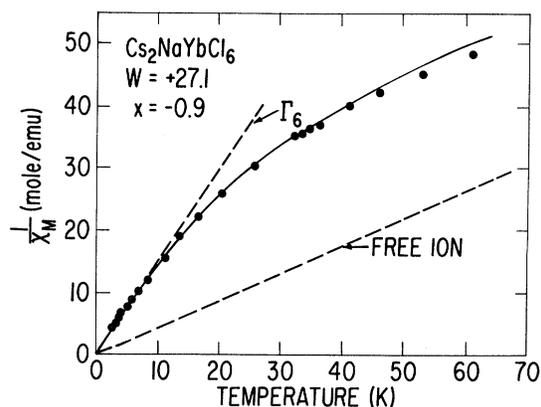

FIG. 10. Measured and calculated susceptibility for $Cs_2NaYbCl_6$.

ated halfway between the R^{3+} and Na^+ ions. Considering only first-neighbor Cl^- contributions to the crystal fields acting on R^{3+}, one obtains within the point-charge model

$$A_4 = 0.4375e^2/d^5 \quad \text{and} \quad A_6 = 0.046\,88e^2/d^7. \tag{12}$$

The lattice constant depends on the particular rare earth considered, varying from $d = 2.6675$ Å $= 5.0425a_0$ for $R = Yb$ to $d = 2.7364$ Å $= 5.17\,27a_0$ for $R = Ce$, where a_0 is the Bohr radius. The results obtained from Eq. (12) are shown by the dashed lines in Fig. 11. The calculation allows a variation of approximately 10% in A_4 and 20% in A_6 in going from Ce to Yb. As one sees from Fig. 11, this is within experimental error. However, the absolute value of A_4 is small by a factor of approximately 5 and A_6 by a factor of 20. A similar discrepancy was previously noted for the Rb_2NaRF_6 compounds as well.[7] Inclusion of more distant neighbors will increase the calculated values somewhat. Carrying the point-charge calculation to fifth neighbors, one obtains $A_4 = 0.5359e^2/d^5$ (an increase of 22%) and $A_6 = 0.050\,28e^2/d^7$ (an increase of 7%). Inclusion of

TABLE II. Crystal-field parameters for the compounds Cs_2NaRCl_6. The quantity W is in units of degree K.

R	J	W	x	Wx	$W(1-|x|)$	Ground state
Ce	$\frac{7}{2}$	334 ± 50	1.0	334 ± 50	0	Γ_7
Nd	$\frac{9}{2}$	-19 ± 7	0.76 ± 0.03	-14.5 ± 4.5	-4.5 ± 2.0	$\Gamma_8^{(2)}$
Tb	6	1.80 ± 0.15	-0.8 ± 0.1	1.53 ± 0.05	-0.3 ± 0.2	Γ_1
Dy	$\frac{15}{2}$	0.92 ± 0.07	-0.63 ± 0.15	-0.58 ± 0.10	0.34 ± 0.15	Γ_6
Ho	8	-1.12 ± 0.25	0.72 ± 0.03	-0.8 ± 0.2	-0.32 ± 0.03	$\Gamma_3^{(2)}$
Tm	6	-2.50 ± 0.25	-0.90 ± 0.15	2.3 ± 0.2	-0.5 ± 0.5	Γ_1
Yb	$\frac{7}{2}$	20 ± 10	-0.85 ± 0.15	25 ± 10	3 ± 3	Γ_6

further neighbors will give a much smaller change.
Use of relativistically calculated values[21] for
$\langle r^4 \rangle$ and $\langle r^6 \rangle$ will increase the calculated para-
meters by roughly 25% for A_4 and 50% for A_6.
Combining these estimates together one obtains
$A_4 \approx 75 a_0^{-4}$ K and $A_6 \approx 0.3 a_0^{-6}$ K. Comparison with

Eq. (11) shows that the point-charge calculation
still provides values which are small compared
to experiment, even for such a well-defined and
presumably ionic system. Inclusion of covalency
effects and accounting for the spatial extent of the
electrons will both increase the calculated values.
For this reason also it is difficult to extrapolate
these results via the point-charge model even to
an isomorphic series of compounds. For example,
previous measurements have been reported for
Rb_2NaYbF_6.[18] In that case, the crystal-field inter-
actions are larger than for $Cs_2NaYbCl_6$. From
the known lattice parameters, Eq. (12) would sug-
gest that the splitting between the ground (Γ_6)
state and the first excited (Γ_8) state for Rb_2NaYbF_6
should be about 2.6 times that for $Cs_2NaYbCl_6$.
Experimentally, the ratio of splittings is observed
to be 1.7, again in poor agreement with the point-
charge model.

IV. CONCLUSIONS

We have interpreted the susceptibility data for
a large number of cubic rare-earth compounds
in terms of simple crystal-field arguments. Good
agreement with the data is found in all cases. The
crystal-field parameters A_4 and A_6 are found to
be approximately independent of the rare-earth
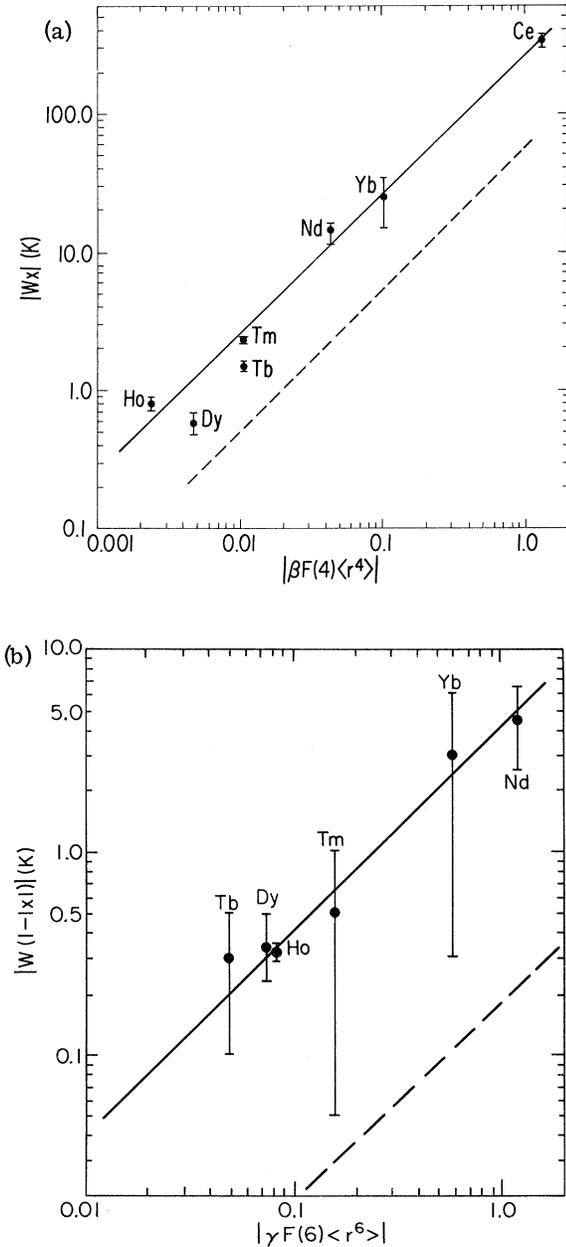ion. By way of summary, we present in Fig. 12

FIG. 11. Dependence on single-ion parameters of the
crystal-field coefficients (a) Wx (proportional to A_4)
and (b) $W(1-|x|)$ (proportional to A_6). Dashed lines
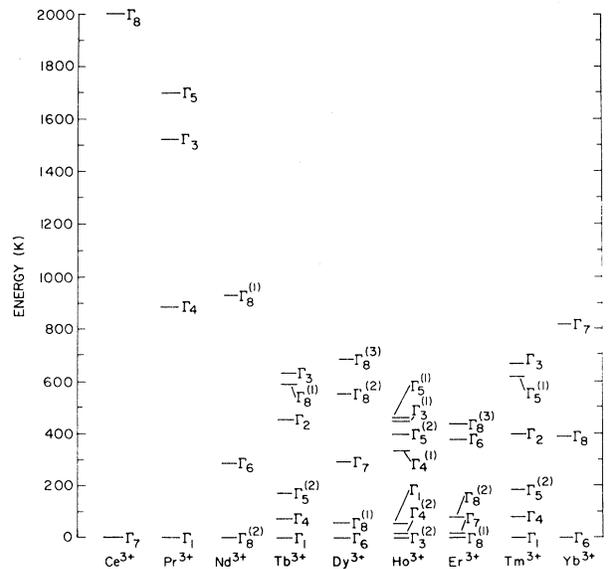show the point-charge prediction.

FIG. 12. Crystal-field splittings using the parameters
of Eq. (11).

crystal-field energies for several rare-earth ions using the experimental A_4 and A_6 values given by Eq. (11). Attempts to explain the observed crystal-field parameters on the basis of a point-charge model are completely unsuccessful.

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