Exact Calculation of the Paramagnetic Susceptibility of a Single Crystal with Arbitrary Crystal Field and Exchange Interactions

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Explicit expressions for the first few terms of the 1/T expansion of the paramagnetic susceptibility are exactly calculated as a function of the parameters of the magnetic Hamiltonian. The calculation is done without approximations such as molecular field. It is done for a single crystal with one kind of magnetic ion in equivalent crystalline sites and can be used when J or S is a good quantum number, or when the lowest energy states can be described using an effective spin S'. The 1/T and $1/T^2$ terms of the susceptibility are calculated as a function of the direction of the applied magnetic field for a crystal with an arbitrary symmetry, dipolar interactions, and arbitrary exchange interactions between the magnetic ions. These interactions, which can give rise to ferromagnetic or antiferromagnetic ordering, may be bilinear, biquadratic or of higher order. The first term of the susceptibility is the well-known C/Tlaw, where C is the Curie constant. Two selection rules allow the determination of the second term which depends only on the bilinear exchange and on the second-order crystal field. The third term and the fourth-order saturation term are calculated in the case of a bilinear exchange for a single crystal having at least three axes of symmetry, where each has at least a twofold symmetry.

I. INTRODUCTION

The exact expressions for the first few terms in the high-temperature series expansion of the paramagnetic susceptibility have been calculated previously under special conditions.¹⁻⁵ This type of series expansion has been calculated in some cases to a very high order in 1/T. Rushbrooke and Wood have determined the first few terms of the paramagnetic susceptibility for isotropic exchange interactions between nearest neighbors only.¹ Daniels⁶ has calculated the paramagnetic susceptibility for effective spin $\frac{1}{2}$ with dipolar interactions. The calculation of Marquard is the most general in that it corresponds to the case of long-range bilinear exchange and second-order single-ion anisotropy.^{7,8} This calculation has been extensively applied to the rare-earth chlorides^{7,8} and rare-earth hydroxides.9,10

The calculation presented here is more general than the above since it starts from a Hamiltonian including arbitrary high-order exchange and arbitrary crystal field terms. The most interesting result of the present calculation is that the secondorder term of the susceptibility (or the constant term of the reciprocal susceptibility) depends only on bilinear exchange and on the second-order crystal field. It had previously been found that, within the molecular-field approximation, this term was dependent only on the second-order coefficients¹¹ of the crystal field. The fact that the second-order term of the susceptibility is dependent on ex-

change only by its bilinear part is the principal new result which is brought out by the present calculation. This selection rule can be very useful. It has been pointed out that for many magnetic crystals the higher-order exchange interactions may be important.^{12, 13} According to the results presented here, they can be disregarded when giving an interpretation of the experimental value of the second-order term of the susceptibility. Using this simplification the theoretical Hamiltonians of rare earths, or a given series of rare-earth compounds, can be studied by comparing the theoretical and experimental variations of the anisotropy of the paramagnetic susceptibility from one rare earth to another; the theoretical variation will depend only on a very small number of parameters.

The previous calculations gave only the initial or zero-field susceptibility. In this paper calculations of the susceptibility in a nonzero magnetic field defined by $\chi(\vec{H}) = \vec{M} \cdot \vec{H}/H^2$ are presented and two saturation terms are found. The first saturation term depends only on the intensity of the magnetic field and is independent of both the single-ion and exchange anisotropy, though in the molecular-field approximation it depended on the effective field.^{11, 14} There is a selection rule for the second saturation term: It depends only on the second- and fourth-order single-ion anisotropy.

In the present calculation the third-order term of the susceptibility is obtained. Its constant part is the sum of four terms. There are two "parasit-

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ic terms" closely related to the expression of the second-order term of the susceptibility which are uninteresting and which are the same as in the molecular-field theory. The two "nonparasitic terms" are (i) the contribution of the crystal potential, as in the molecular-field approximation,¹¹ and (ii) a contribution of exchange, which is the same as found by Marquard^{7, 8} and which does not exist in the molecular-field approximation. The latter term corresponds, for an isotropic crystal, to the first deviation from the Curie-Weiss law.

II. GENERAL EXPRESSION OF HAMILTONIAN

There are two kinds of interactions between the magnetic ions in a crystal: the electrostatic and magnetic interactions. The magnetic interactions are dipolar interactions. The former can be divided into Coulomb and exchange interactions. When J (or S) is a good quantum number (rare earths, Fe^{3+} , or Mn^{2+}), the crystal field, which is the anisotropic part of the Coulomb interaction, can be expressed as a function of the Stevens operator equivalents, $O_l^{mc}(\mathbf{J})$ and $O_l^{ms}(\mathbf{J})$, ¹⁵ which are functions of \mathbf{J} and are proportional to the real and imaginary parts of the spherical harmonics within a J manifold. We shall call μ the set of two indices mc or ms. The exchange interaction between two ions can be expressed as a function of the ${ar J}$ of the two ions and, since the $O_t^{\mu}(\mathbf{J})$ form a complete basis set of functions of J, it can be expressed as a bilinear function of the Stevens operator equivalents relative to the two ions.¹² Then, when J or S is a good quantum number, the most general form for the Hamiltonian of the magnetic ions is

$$3C = \sum_{\substack{(i_j), i \neq j \\ k \neq j}} \sum_{\substack{I(i), \mu(i) \\ k \neq j}} \sum_{\substack{I(j), \mu(j) \\ \mu(i)I(j) \\ \mu(j) \end{pmatrix}} \sum_{\substack{(j), \mu(j) \\ I(j) \\ \mu(k) \end{pmatrix}} \sum_{\substack{(j), \mu(k) \\ I(k) \end{pmatrix}} \sum_{\substack{(j), \mu(k) \\ I(k) \end{pmatrix}} \sum_{\substack{(j), \mu(k) \\ \mu(k) } \sum_{\substack{(j), \mu(k) \\ \mu(k) \end{pmatrix}} \sum_{\substack{(j), \mu(k) \\ \mu(k) } } \sum_{\substack{(j), \mu(k) \\ \mu(k) } \sum_{\substack{(j), \mu(k) \\ \mu(k) } } \sum_{\substack{(j), \mu(k) \\ \mu(k) } } \sum_{\substack{(j), \mu(k) \\ \mu(k) } \sum_{\substack{(j), \mu(k) \\ \mu(k) } } \sum_{\substack{(j), \mu(k) \\ \mu(k) } } \sum_{\substack{(j), \mu(k) \\ \mu(k) } \sum_{\substack{(j), \mu(k) \\ \mu(k) } } \sum_{\substack{(j), \mu(k) \\ \mu(k) } } \sum_{\substack{(j), \mu(k) \\ \mu(k) } \sum_{\substack{(j), \mu(k) \\ \mu(k) } } \sum_{\substack{(j), \mu(k) \\ \mu(k) } } \sum_{\substack{(j), \mu(k) \\ \mu(k) } } \sum_{\substack{(j), \mu(k) } } \sum_{\substack{(j), \mu(k) \\$$

where the index *i* means the ion *i*; in the first summation each pair of sites occurs only once. In this expression g_J is the Landé factor, μ_B the Bohr magneton, and \vec{H} the applied magnetic field. The first term of the Hamiltonian represents the exchange interactions, the second the crystal field, the third the Zeeman term, and \mathcal{K}_d the dipolar interactions. We shall assume that there is only one kind of magnetic ion in one crystalline site. Then the coefficients $n_{ifl}(i)\mu(i)I(j)\mu(j)$ are dependent only on the relative positions of the two magnetic ions and the $u_{I(k)}^{\mu(k)}$ are identical for all the ions. We have $n_{ifl}(i)\mu(i)I(j)\mu(j) = n_{ifl}(j)\mu(j)I(i)\mu(i)$ because the two coefficients have the same meaning. The roles of the ions *i* and *j* are symmetrical and $n_{ijl(i)\mu(i)l(j)\mu(j)} = n_{ijl(j)\mu(j)l(i)\mu(i)}$.

The Hamiltonian has the following properties. The only nonzero terms correspond to $l(i) \leq 2l+1$ and $l(j) \leq 2l+1$, where *l* is the orbital quantum number of one of the magnetic electrons¹² and $l(k) \leq 2l$. For rare earths, l=3. If \tilde{J} is changed into $-\tilde{J}$, $O_l^{\mu}(\tilde{J})$ is changed into $(-1)^l O_l^{\mu}(\tilde{J})$. The Hamiltonian is invariant under time reversal. Then l(i) and l(j) must be of the same parity, and l(k) is even.

The lowest exchange terms correspond to $l_i = l_j$ = 1. They represent the bilinear exchange. x, y, z is a right-handed orthonormal basis. When \vec{z} is the quantization axis $O_1^0(\vec{J}) = J_z$, $O_1^{1o}(\vec{J}) = J_x$, $O_1^{1s}(\vec{J})$ = J_y . When there is only bilinear exchange, the Hamiltonian can be written

$$\mathcal{C} = \sum_{(ij)\ i\neq j} \mathbf{\tilde{J}}_{i} \cdot \mathbf{\tilde{n}}_{ij} \cdot \mathbf{\tilde{J}}_{j} + \sum_{k} \sum_{l(k)\mu(k)} u_{l(k)}^{\mu(k)} O_{l(k)}^{\mu(k)} (\mathbf{\tilde{J}}_{k}) - \sum_{k'} g_{J} \mu_{B} \mathbf{\tilde{J}}_{k'} \cdot \mathbf{\tilde{H}} + \mathcal{K}_{0} .$$
(2)

The components of the exchange tensor \overline{n}_{ij} are related to the coefficients defined in (1) by $n_{ijzz} = n_{ij1010}$, $n_{ijzx} = n_{ij1011c}$, etc. Since there is one kind of magnetic ion in one crystalline site, $n_{ijxy} = n_{ijyx}$, etc. The tensor \overline{n}_{ij} is symmetric and there is no Dzyaloshinskii term.

III. METHOD OF CALCULATION

The magnetization of a state $|h\rangle$ of the crystal is $\vec{\mathbf{M}}_{h} = g_{J}\mu_{B}\langle h|\Sigma_{i} \vec{\mathbf{J}}_{i}|h\rangle$. If $|h\rangle$ is an eigenstate of the Hamiltonian associated with the energy W_{h} , then $\vec{\mathbf{M}}_{h} = -\vec{\nabla}_{\vec{\mathbf{H}}}(W_{h})$ when referred to axes linked to the crystal.¹⁶ At temperature *T*, the magnetization of the crystal is

$$\vec{\mathbf{M}} = \frac{-\sum_{h} \vec{\nabla}_{\vec{\mathbf{H}}} (W_{h}) e^{-W_{h}/kT}}{\sum_{h} e^{-W_{h}/kT}} \quad .$$
(3)

When replacing the exponentials by the first terms of their 1/T expansions one obtains the first terms of the expansion of \vec{M} .

All the terms in the expansion of the magnetization are proportional to expressions of the type $\sum_h W_h^n$ or to derivatives of such expressions: $\sum_{h} W_{h}^{n} = \operatorname{Tr}_{cr} \mathcal{H}^{n}$. \mathcal{H} is the Hamiltonian of all the magnetic ions. Tr_{cr} is the trace over all the space of the entire wave function for all the magnetic ions of the crystal. When the Hamiltonian ${\boldsymbol{\mathfrak{K}}}$ is expressed as a bilinear function of the Stevens operator equivalents, then $\operatorname{Tr}_{\operatorname{cr}} \mathcal{H}^n$ is a sum of traces of products of spherical harmonics acting on different ions, some of them acting sometimes on the same ion. Such a product of spherical harmonics can be written $\prod_{i} f(i)$, where f(i) is an operator acting on the ion *i*. Since the trace of the identity operator on a given ion is 2J+1, we have the relation

$$\Gamma \mathbf{r}_{\mathrm{cr}} \left(\prod_{i} f(i) \right) = (2J+1)^{N-\Sigma_{i}} \prod_{i} \mathrm{Tr}_{\mathrm{io}}[f(i)], \qquad (4)$$

where N is the number of magnetic ions of the crystal, *i* is the number of the ions corresponding to the operators f(i), and $\operatorname{Tr}_{io}[f(i)]$ is the trace of the single-ion operator f(i) associated with the corresponding ion *i*. By using relation (4) for our particular problem, we transform traces on the whole crystal into traces of single-ion \overline{J} functions that are easy to calculate.

I had previously established¹¹ that

$$\operatorname{Tr}_{\mathbf{i}0}\left[O_{1}^{\mu}(\mathbf{\bar{J}})\right] = 0 , \qquad (5)$$

except for l=0, because this trace must vary both as \mathfrak{D}_l and \mathfrak{D}_0 . As a result, we have the following two particular cases of (4) which are often used in our calculation:

$$\operatorname{Tr}_{\mathrm{cr}}\begin{bmatrix}\mu(i)\\O_{I(i)}(\mathbf{\tilde{J}}_{i})\end{bmatrix} = (2J+1)^{N-1}\operatorname{Tr}_{\mathrm{io}}[O_{I}^{\mu}(\mathbf{\tilde{J}})] = 0 \quad (6)$$

for $l \neq 0$ and

$$\operatorname{Tr}_{\mathrm{cr}} \begin{bmatrix} \mu(i) & \mu(j) \\ O_{I(i)}(\mathbf{\tilde{J}}_{i}) & O_{I(j)}(\mathbf{\tilde{J}}_{j}) \end{bmatrix} = (2J+1)^{N-2}$$
$$\times \operatorname{Tr}_{\mathrm{io}} \begin{bmatrix} \mu(i) \\ O_{I(i)}(\mathbf{\tilde{J}}) \end{bmatrix} \operatorname{Tr}_{\mathrm{io}} \begin{bmatrix} \mu(j) \\ O_{I(j)}(\mathbf{\tilde{J}}) \end{bmatrix} = 0$$
$$\operatorname{if} i \neq j, \ l_{i} \neq 0, \ l_{j} \neq 0 \ . \tag{7}$$

If the two operators act on the same ion i then¹¹

$$\operatorname{Tr}_{cr} \begin{bmatrix} \mu(i) & \mu(j) \\ O_{I(i)}(\overline{J}_{i}) & O_{I(j)}(\overline{J}_{j}) \end{bmatrix}$$
$$= (2J+1)^{N-2} \operatorname{Tr}_{io} \begin{bmatrix} \mu(i) & \mu(j) \\ O_{I(i)}(\overline{J}) & O_{I(j)}(\overline{J}) \end{bmatrix} \propto \delta_{I_{1}-I_{2}\mu_{1}\mu_{2}} .$$
(8)

IV. SUSCEPTIBILITY TO SECOND ORDER IN 1/T

In the 1/T expansion of (3) the first term in the denominator is $\sum_{h} 1 = (2J+1)^{N}$, since there exist $(2J+1)^{N}$ orthonormal states in the crystal. In the expansion of \vec{M} there are terms which contain $\sum_{h} W_{h} = \operatorname{Tr}_{cr}(\mathcal{H})$. If we drop from the Hamiltonian the constant terms corresponding to l=0, we deduce from Eqs. (6) and (7) that

$$\sum_{h} W_{h} = 0$$
 (9)

Equation (3) then becomes

$$M_{g} = \frac{1}{(2J+1)^{N}} \frac{\sum_{h} [\partial(W_{h}^{2})/\partial H_{g}]}{2kT} - \frac{1}{(2J+1)^{N}} \frac{\sum_{h} [\partial(W_{h}^{3})/\partial H_{g}]}{6k^{2}T^{2}} + O\left(\frac{1}{T^{3}}\right) .$$
(10)

A. Derivation of First Term

We can write $\Re = \Re_{ex} + V + \Re_z$, where \Re_{ex} is the exchange part of the Hamiltonian, V is the crystalline potential, and \Re_z the Zeeman term. The

dipolar term is included in the bilinear-exchange term. We shall display in Sec. VI the contribution of the dipolar term to the susceptibility. \vec{M} must be an odd function of \vec{H} . Then only the term of order two in \vec{H} of $\sum_{h} W_{h}^{2} = \operatorname{Tr}_{cr}(\mathcal{K}^{2})$ can give a contribution to \vec{M} . This term is

$$\operatorname{Tr}_{\mathrm{cr}}(\mathcal{B}_{Z}^{2}) = g_{J}^{2} \mu_{B}^{2} \operatorname{Tr}_{\mathrm{cr}}\left(\sum_{i} (\mathbf{\tilde{J}}_{i} \cdot \mathbf{\tilde{H}}) \sum_{j} (\mathbf{\tilde{J}}_{j} \cdot \mathbf{\tilde{H}})\right)$$

Since $Tr(\bar{J}) = 0$, the only nonzero terms correspond to i = j and

$$\operatorname{Tr}_{cr}(\mathcal{B}_{z}^{2}) = N(2J+1)^{N-1}g_{J}^{2}\mu_{B}^{2}\operatorname{Tr}_{io}[(\mathbf{\bar{J}}\cdot\mathbf{\bar{H}})^{2}]$$
.

This trace being independent of the direction of \vec{H} , we can take $\vec{H} \parallel \vec{z}$. Then

$$Tr_{io}[(\vec{J} \cdot \vec{H})^{2}] = H^{2}Tr_{io}(J_{z}^{2}) = \frac{1}{3}J(J+1)(2J+1)H^{2},$$

$$Tr_{or}(\mathcal{K}_{z}^{2}) = N(2J+1)^{N}g_{J}^{2}\mu_{B}^{2}\frac{1}{3}J(J+1)H^{2}.$$
(11)
B. Second Term

Since $\overline{\mathbf{M}}$ is an odd function of $\overline{\mathbf{H}}$, the only terms of $\sum_{h} W_{h}^{3}$ which give a contribution are the terms of second order in $\overline{\mathbf{H}}$. They are

$$\operatorname{Tr}_{\operatorname{cr}}\left(\sum_{\operatorname{perm}} V\mathcal{H}_{Z}^{2}\right)$$
, $\operatorname{Tr}_{\operatorname{cr}}\left(\sum_{\operatorname{perm}} \mathcal{H}_{\operatorname{ex}}\mathcal{H}_{Z}^{2}\right)$

where \sum_{perm} denotes the sum over all permutations of the operator V or \mathcal{H}_{ex} with the two operators \mathcal{H}_z . A cyclical permutation of operators does not change the trace, and we have

$$\begin{aligned} \mathrm{Tr}_{\mathrm{cr}} & \left(\sum_{\mathrm{perm}} V \mathcal{H}_{Z}^{2} \right) = 3 \mathrm{Tr}_{\mathrm{cr}} \left(V \mathcal{H}_{Z}^{2} \right) , \\ \mathrm{Tr}_{\mathrm{cr}} & \left(\sum_{\mathrm{perm}} \mathcal{H}_{\mathrm{ex}} \mathcal{H}_{Z}^{2} \right) = 3 \mathrm{Tr}_{\mathrm{cr}} \left(\mathcal{H}_{\mathrm{ex}} \mathcal{H}_{Z}^{2} \right) . \\ & I. \ Calculation \ of \ Tr_{\mathrm{cr}} \left(\mathcal{V} \mathcal{H}_{Z}^{2} \right) \end{aligned}$$

We have

$$\begin{aligned} \operatorname{Tr}_{\mathrm{cr}}(V \mathcal{H}_{Z}^{2}) &= g_{J}^{2} \mu_{B}^{2} \sum_{k} \sum_{l(k) \mu(k)} \sum_{l(k) \mu(k)} \sum_{k'} \sum_{k'} u_{1(k)}^{\mu(k)} \\ &\times \operatorname{Tr}_{\mathrm{cr}}\left[O_{1(k)}^{\mu(k)}(\overline{\mathbf{J}}_{k}) (\overline{\mathbf{J}}_{k'} \cdot \overline{\mathbf{H}}) (\overline{\mathbf{J}}_{k'} \cdot \overline{\mathbf{H}})\right] \end{aligned}$$

Since $\operatorname{Tr}(\overline{\mathbf{J}}) = 0$ and $\operatorname{Tr}[O_l^{\mu}(\overline{\mathbf{J}})] = 0$, the only nonzero terms correspond to k = k' = k'' and

$$\operatorname{Tr}_{\mathrm{cr}}(V\mathcal{H}_{Z}^{2}) = Ng_{J}^{2} \,\mu_{B}^{2} (2J+1)^{N-1} \operatorname{Tr}_{\mathrm{io}}\left[V(\mathbf{\bar{J}}\cdot\mathbf{\bar{H}})^{2}\right]$$

In a rotation, the components of \overline{J} transform into one another according to the \mathfrak{D}_1 representation of the rotation group. All of the nine operators J_x^2 , J_y^2 , J_x^2 , $(J_x J_y + J_y J_x)$, etc. therefore transform into one another according to the representation \mathfrak{D}_1 $\times \mathfrak{D}_1 = \mathfrak{D}_0 + \mathfrak{D}_1 + \mathfrak{D}_2$. Since these nine operators are symmetrical, they transform into one another as $\mathfrak{D}_0 + \mathfrak{D}_2$. Let V_{2n} be the part of V of order 2n in the Stevens operator equivalents. V_{2n} transforms as \mathfrak{D}_{2n} , and $\operatorname{Tr} [V_{2n} (J_\alpha J_\beta + J_\beta J_\alpha)]$, where α and β are x, y, or z transforms as $\mathfrak{D}_{2n} \times (\mathfrak{D}_2 + \mathfrak{D}_0)$ when the operators rotate and the dynamical states do not

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rotate. A trace is invariant and $\mathfrak{D}_{2n} \times (\mathfrak{D}_2 + \mathfrak{D}_0)$ contains \mathfrak{D}_0 only if n = 0 or 1. If we drop the constant term of V, the only term giving a nonzero trace is V_2 :

$$\operatorname{Tr}_{io}\left[V(\mathbf{\bar{J}}\cdot\mathbf{\bar{H}})^{2}\right] = \operatorname{Tr}_{io}\left[V_{2}(\mathbf{\bar{J}}\cdot\mathbf{\bar{H}})^{2}\right].$$
(12)

We have demonstrated the first selection rule: The magnetization depends only on the second-order crystal field parameters to second order in the reciprocal temperature.

The expression of V_2 as a function of the Stevens equivalent operators is

$$V_{2} = \left[3J_{g}^{2} - J(J+1)\right]u_{2g}^{0} + \left(J_{x}^{2} - J_{y}^{2}\right)u_{2g}^{2c} + \left(J_{x}J_{y} + J_{y}J_{x}\right)u_{2g}^{2s} + \left(J_{y}J_{z} + J_{z}J_{y}\right)u_{2g}^{1s} + \left(J_{z}J_{x} + J_{x}J_{z}\right)u_{2g}^{1c}, \quad (13)$$

when z is the quantization axis. We can also write

$$V_{2} = u_{xx}J_{x}^{2} + u_{yy}J_{y}^{2} + u_{zz}J_{z}^{2} + u_{xy}(J_{x}J_{y} + J_{y}J_{x}) + u_{yz}(J_{y}J_{z} + J_{z}J_{y}) + u_{zx}(J_{z}J_{x} + J_{x}J_{z}) - \frac{1}{3}J(J+1)(u_{wx} + u_{wy} + u_{zz}), \quad (14)$$

the constant term being determined by $Tr(V_2) = 0$. It can easily be seen that V_2 is unchanged if we add simultaneously to u_{xx} , u_{yy} , and u_{zz} a given arbitrary constant. We can choose the constant such that

$$u_{xx} + u_{yy} + u_{zz} = 0 \tag{15}$$

and

$$V_{2} = u_{xx}J_{x}^{2} + u_{yy}J_{y}^{2} + u_{zz}J_{z}^{2} + u_{xy}(J_{x}J_{y} + J_{y}J_{x}) + u_{yz}(J_{y}J_{z} + J_{z}J_{y}) + u_{zx}(J_{z}J_{x} + J_{x}J_{z}) .$$
(16)

We see in Eq. (16) that the left and right products of the vector \mathbf{J} with the symmetrical matrix of elements u_{ij} are a given operator independent of the coordinate axes. Then the u_{ij} are the components of a symmetrical tensor \mathbf{u} . According to (15) \mathbf{u} is traceless and transforms in the D_2 representation. V_2 can be written

$$V_2 = \mathbf{J} \cdot \mathbf{u} \cdot \mathbf{J} . \tag{17}$$

Using the properties of \tilde{J} , we obtain the equivalent expression

$$V_{2} = [3J_{z}^{2} - J(J+1)] \frac{u_{zz}}{2} + \frac{1}{2} (u_{xx} - u_{yy}) (J_{x}^{2} - J_{y}^{2}) + u_{xy} (J_{x} J_{y} + J_{y} J_{x}) + u_{yz} (J_{y} J_{z} + J_{z} J_{y}) + u_{zx} (J_{z} J_{x} + J_{x} J_{z}) .$$
(18)

By identification of (13) and (18) we obtain the relations

$$u_{zz} = 2u_{2z}^{0} ,$$

$$u_{xx} = 2u_{2x}^{0} = u_{2z}^{2c} - u_{2z}^{0} ,$$

$$u_{yy} = 2u_{2y}^{0} = -u_{2z}^{2c} - u_{2z}^{0} ;$$

(19)

$$u_{xy} = u_{2z}^{2s} , \quad u_{yz} = u_{2z}^{1s} , \quad u_{xx} = u_{2z}^{1c} , u_{2x}^{0} + u_{2y}^{0} + u_{2z}^{0} = 0 ,$$
(20)

where $u_{2\alpha}^0$ is the coefficient of $O_2^0(\vec{J})$ of V_2 when $\vec{\alpha}$ is the quantization axis.

We know that a trace of a product of powers of J_x , J_y , and J_z is nonzero only if the product has the same parity in J_x , J_y , J_z . Then we have

$$\operatorname{Tr}\left[V_{2}(\mathbf{\vec{J}}\cdot\mathbf{\vec{H}})^{2}\right] = \sum_{\beta} H_{\beta}^{2} \sum_{\alpha} u_{\alpha\alpha} \operatorname{Tr}\left(J_{\alpha}^{2}J_{\beta}^{2}\right) + \sum_{(\alpha\beta)\alpha\neq\beta} \operatorname{Tr}\left[(J_{\alpha}J_{\beta}+J_{\beta}J_{\alpha})^{2}\right].$$

When we express the traces as functions of J,¹⁷ we obtain

$$\operatorname{Tr}_{io}\left[V_{2}(\mathbf{J}\cdot\mathbf{\hat{H}})^{2}\right] = \frac{J(J+1)\left(2J+1\right)\left(2J-1\right)\left(2J+3\right)}{30}\,\mathbf{\hat{H}}\cdot\mathbf{\vec{u}}\cdot\mathbf{\hat{H}} \qquad (21)$$

and

$$\Gamma \mathbf{r}_{cr} (V \mathcal{K}_Z^2) = N g_J^2 \mu_B^2 (2J+1)^N$$

$$\times \frac{J(J+1)(2J-1)(2J+3)}{30} \vec{H} \cdot \vec{u} \cdot \vec{H} .$$
 (22)

2. Calculation of
$$Tr_{cr}(\mathcal{H}_{ex}\mathcal{H}_Z^2)$$

This trace is a linear function of traces of the general form

$$\operatorname{Tr}_{\operatorname{cr}}\left[O_{l(i)}^{\mu(i)}(\ddot{\mathbf{J}}_{i})O_{l(j)}^{\mu(j)}(\ddot{\mathbf{J}}_{j})(\ddot{\mathbf{J}}_{k'}\cdot\dot{\mathbf{f}})(\ddot{\mathbf{J}}_{k'}\cdot\dot{\mathbf{f}})\right],$$

with $i \neq j$. Since Tr $[O_i^{\mu}(\vec{J})] = 0$, the only nonzero terms correspond to k' = i, k'' = j or k' = j, k'' = i; using relation (4), we have

$$\begin{aligned} \operatorname{Tr}_{\operatorname{cr}}(\operatorname{\mathcal{GC}}_{\operatorname{ex}} \operatorname{\mathcal{C}}_{Z}^{2}) &= 2g_{J}^{2} \mu_{B}^{2} (2J+1)^{N-2} \\ & \times \sum_{(ij)i \neq j} \sum_{I(i) \mu(i)} \sum_{I(j) \mu(j)} n_{ijI(i) \mu(i)I(j) \mu(j)} \\ & \times \operatorname{Tr}_{\operatorname{io}} \left[O_{I(i)}^{\mu(i)}(\overline{\mathbf{J}}_{i}) (\overline{\mathbf{J}}_{i} \cdot \overline{\mathbf{H}}) \right] \times \operatorname{Tr}_{\operatorname{io}} \left[O_{I(i)}^{\mu(j)}(\overline{\mathbf{J}}_{i}) (\overline{\mathbf{J}}_{i} \cdot \overline{\mathbf{H}}) \right] \end{aligned}$$

The components of \overline{J} belong to \mathfrak{D}_1 , and $\mathfrak{D}_1 \times \mathfrak{D}_1$ contains \mathfrak{D}_0 only if l=1. Then the only traces which are nonzero correspond to $l_i = l_j = 1$.

We have demonstrated the second selection rule: The magnetization depends only on bilinear exchange to second order in the reciprocal temperature.

When expressed with the tensorial expression for bilinear exchange [Eq. (2)], the expression for $\operatorname{Tr}_{cr}(\mathfrak{K}_{ex}\mathfrak{K}_{z}^{2})$ can be written

$$\mathbf{Tr}_{\mathbf{cr}}(\mathcal{K}_{\mathbf{ex}}\mathcal{K}_{Z}^{2}) = 2 g_{J}^{2} \mu_{B}^{2} (2J+1)^{N-2} \sum_{(ij)i \neq j} \sum_{\alpha,\beta} n_{ij\alpha\beta} \\ \times \mathbf{Tr}_{io} [J_{\alpha}(\mathbf{\bar{J}} \cdot \mathbf{\bar{H}})] \times \mathbf{Tr}_{io} [J_{\beta}(\mathbf{\bar{J}} \cdot \mathbf{\bar{H}})] .$$
(23)

Let us define $\overrightarrow{\mathbf{N}} = \sum_{(ij)i \neq j} \overrightarrow{\mathbf{n}}_{ij}$. Since we have $\operatorname{Tr}(J_{\alpha}J_{\beta}) = \frac{1}{3}J(J+1)(2J+1)\delta_{\alpha\beta}$, we find

(24)

C. Expressions and Properties of Magnetization and Susceptibility

Using Eqs. (11), (22), and (24), we obtain from Eq. (10) the explicit expression of the magnetization,

$$\vec{\mathbf{M}} = \frac{C}{T} \left(\vec{\mathbf{H}} - \frac{2J(J+1)}{3NkT} \quad \vec{\mathbf{N}} \cdot \vec{\mathbf{H}} - \frac{(2J-1)(2J+3)}{10kT} \quad \vec{\mathbf{u}} \cdot \vec{\mathbf{H}} \right) + O\left(\frac{1}{T^3}\right) \quad . \tag{25}$$

 $C = Ng_J^2 \mu_B^2 J(J+1)/3k$ is the atom gram Curie constant when N is the Avogadro number. The susceptibility, defined by $\chi = (\vec{M} \cdot \vec{H}/H^2)$, is

$$\chi = \frac{C}{T} \left(1 - \frac{2J(J+1)}{3NkT} - \frac{\vec{H} \cdot \vec{N} \cdot \vec{H}}{H^2} - \frac{(2J-1)(2J+3)}{10kT} - \frac{\vec{H} \cdot \vec{u} \cdot \vec{H}}{H^2} + O\left(\frac{1}{T^3}\right) + O\left(\frac{1}{T^3}\right) \right)$$
(26)

The two selection rules are in evidence in the expression for the susceptibility; the exchange is represented only by the tensor \overline{N} , which is the sum over all the pairs of magnetic ions of the bilinear-exchange tensors, and the crystal field only by the tensor \vec{u} , whose elements are the coefficients of the second-order term of the crystal field. The susceptibility is a linear function of the bilinear-exchange and crystal field parameters and is a quadratic function of the direction cosines of the magnetic field, but is independent of its intensity. Since there is one kind of magnetic ion in one crystalline site, we have also $\overline{N} = \frac{1}{2}N\sum_{i\neq 1}\overline{n}_{1i}$: The tensor \overline{N} is proportional to the sum of the exchange-interaction tensors between one ion and all the others.

In the screened point-charge model, when the magnetic ions are rare-earth ions, if q_r is the charge of one ion in the sublattice r of the crystal and c_r the screening coefficient relative to this sublattice, we have¹⁵

$$u_{\alpha\beta} = -\frac{3|e|}{2} \alpha_J \langle r^2 \rangle \sum_r c_r q_r \sum_{i \in r} \frac{\alpha_i \beta_i - (r_i^2/3) \delta_{\alpha_i \beta_i}}{r_i^5}$$
(27)

In the above equation e is the charge of the electron, $\langle r^2 \rangle$ is the average value of the square of the distance between a 4f electron and the nucleus of the ion, α_i is one of the coordinates of the *i*th ion, r_i is its distance from the origin, and α_j is a coefficient tabulated in Ref. 15. Freeman and Watson have calculated $\langle r^2 \rangle$ for the 4f electrons of rare earths.¹⁸

The reciprocal susceptibility is given by

$$\frac{1}{\chi} = \frac{1}{C} \left(T + \frac{2J(J+1)}{3Nk} \quad \frac{\vec{H} \cdot \vec{N} \cdot \vec{H}}{H^2} \right)$$

$$+\frac{(2J-1)(2J+3)}{10k} \frac{\vec{\mathrm{H}}\cdot\vec{\mathrm{u}}\cdot\vec{\mathrm{H}}}{H^2} + O\left(\frac{1}{T}\right) \quad . \tag{28}$$

We shall show in Sec. VIIIB that the 1/T term is relatively small when the relative anisotropy of the susceptibility is at most approximately one. In a first approximation the reciprocal susceptibilities corresponding to various directions of the magnetic field are parallel straight lines whose slope is 1/C.

Expression (28) for $1/\chi$ is the same as the expression obtained in the molecular-field approximation in the presence of bilinear exchange.¹¹ But in the molecular-field theory we could not calculate the contribution of the higher-order exchange terms, whereas with the exact calculation we have established that the contribution of these terms is zero.

Expressions (26) and (28) both give a quadratic variation of χ and $1/\chi$ with the direction cosines of the magnetic field. If the relative anisotropy of the susceptibility is important, χ and $1/\chi$ cannot both be quadratic functions of the direction cosines of the field. Expression (26) for χ is independent of the intensity of the magnetic field and is valid for a weak magnetic field. When \vec{H} is small, \vec{M} is small and only an expansion of \vec{M} or χ or of the free energy \mathfrak{F} with respect to \vec{H} has meaning. Since $\vec{M} = -\vec{\nabla}_{\vec{H}} \mathfrak{F}$ (Ref. 16)

$$\chi = -\frac{1}{H^2} \sum_{\alpha\beta} \frac{\partial^2 \mathfrak{F}}{\partial H_\alpha \,\partial H_\beta} H_\alpha H_\beta .$$

Then for a weak magnetic field, the angular variation of χ is the correct one. The initial susceptibility always varies exactly quadratically with the direction cosines of the applied magnetic field. and the susceptibility has practically the same angular variation when it is very close to the initial susceptibility. Experimentally, it is generally the case and we shall show in Sec. VIII B that, in agreement with the experimental results, the first saturation terms are small in typical magnetic fields. For instance, in rare earths where the relative anisotropy of the susceptibility is important, the susceptibility varies quadratically with the direction cosines of the magnetic field.¹⁹ In expression (28) for $1/\chi$, the complementary term is certainly not negligible for some directions of the applied magnetic field.

When the crystal has at least three axes of symmetry of at least second order, they will also be the common axes of symmetry of the tensors \vec{N} and \vec{u} . The reciprocal susceptibility along one of these symmetry axes \vec{x} , \vec{y} , or \vec{z} will be

$$\frac{1}{\chi_{\alpha}} = \frac{1}{C} \left(T + \frac{2J(J+1)}{3Nk} N_{\alpha\alpha} + \frac{(2J-1)(2J+3)}{10k} u_{\alpha\alpha} \right) + O\left(\frac{1}{T}\right) .$$
(29)

This more simple expression will be adequate for most experimental situations, since most of the crystals with one kind of magnetic ion in one crystalline site have three axes of symmetry.

When the exchange energy is more important than the crystal field energy, we shall see in Sec. VIII B that the convergence of the reciprocal susceptibility is more rapid than that of the susceptibility. In this case, which corresponds in particular to heavy rare-earth (from Gd to Er) single crystals, it is better to use expression (29) for $1/\chi$ along the symmetry axes. Along other directions the susceptibility will be given by

$$\chi = \chi_x \,\alpha_H^2 + \chi_y \beta_H^2 + \chi_z \gamma_H^2 \,, \tag{30}$$

where α_H , β_H , γ_H are the direction cosines of the magnetic field. For most insulators with rareearth ions, the crystal field energy is more important than the exchange interaction, and it is better to use the expansion of χ for an arbitrary direction.

The Curie temperature along one of the symmetry axes is

$$\Theta_{p\alpha} = -\frac{2J(J+1)}{3Nk} N_{\alpha\alpha} - \frac{(2J-1)(2J+3)}{10k} u_{\alpha\alpha} . \quad (31)$$

When the crystal is cubic, the susceptibility cannot vary with the squares of the direction cosines of the magnetic field and is therefore isotropic; $N_{xx} = N_{yy} = N_{zz}$ and $u_{\alpha\alpha} = 0$.

V. APPLICATION TO RARE-EARTH SINGLE CRYSTALS

Rare-earth metals have hexagonal symmetry. Heavy rare earths (gadolinium, terbium, dysprosium, holmium, erbium) have ordering temperatures between 85 K (erbium) and 293 K (gadolinium). There is a very strong magnetocrystalline anisotropy between the basal plane and the sixfold c axis. There is an important anisotropy of the susceptibility¹⁹ except for gadolinium, which is in an S state and has therefore a small anisotropy.

If we take \vec{z} parallel to the *c* axis and \vec{x} , \vec{y} in the basal plane, Eq. (29) can be written in this particular case, using (19) and (20),

$$\frac{1}{\chi_{z}} = \frac{1}{C} \left(T + \frac{2J(J+1)}{3Nk} N_{zz} + \frac{(2J-1 \quad (2J+3)}{5k} u_{2z}^{0} \right) + O\left(\frac{1}{T}\right) , \quad (32)$$

$$\frac{1}{\chi_{y}} = \frac{1}{\chi_{x}} = \frac{1}{C} \left(T + \frac{2J(J+1)}{3Nk} N_{xx} - \frac{(2J-1) \quad (2J+3)}{10k} u_{2z}^{0} \right) + O\left(\frac{1}{T}\right) .$$

The susceptibility in other directions is given by (30). Experimentally, the thermal variations of the susceptibilities are represented by almost parallel straight lines whose slopes are close to 1/C. This is in agreement with the fact that the

1/T term is expected to be small, as developed later in Sec. VIII B. The experimental data on the anisotropy of the susceptibility give one equation with two unknown variables: $N_{zz} - N_{xx}$, which represents the contribution of the exchange anisotropy, and u_{2z}^0 , the contribution of the single-ion anisotropy. Equations (32) are identical to the one encountered in the molecular-field approximation. I had already established these equations within this approximation in a previous article,¹¹ and from the measurement of $1/\chi_z$ and $1/\chi_x$ by Aléonard, I had deduced the thermal variation of the parameter u_{2z}^0 (with the assumption of a small exchange anisotropy) for Tb, Dy, Ho, and Er.¹⁹

A. Determination of Contributions of Single-Ion and Exchange Anisotropy from a Theoretical Hamiltonian

We can use the new selection rule according to which the paramagnetic susceptibility depends only on the bilinear-exchange terms to obtain new information from the experimental data.

The theoretical exchange Hamiltonians established for rare earths (see Refs. 20-22 and references included there) contain bilinear-exchange and higher-order exchange terms. The anisotropy of the paramagnetic susceptibility will depend only on the bilinear-exchange parameter and on the parameter u_{2z}^0 . In the screened point-charge model the variation of u_{2x}^0 from one rare earth to another is known, since it is imposed by group theory [it corresponds to the variation of the coefficient α_J of Eq. (27)]. The variation of the bilinear-exchange parameter from one rare earth to another is imposed by the theoretical Hamiltonian and is different from the variation of u_{2z}^0 . From a comparison between the experimental values of the anisotropy of the susceptibility for the different rare earths, we could separate the contribution of the singleion anisotropy from that of the exchange anisotropy. For this study, we need very accurate experimental data,²³ and we must take in account very carefully the variation of the lattice parameters from one rare earth to another, the thermal expansion, and magnetostriction effects.^{19,24} The experimental variation of the anisotropy of the paramagnetic Curie temperature from one rare earth to another is not very different from that of $u_{2\pi}^0$, except for holmium and erbium.²⁵ It can be due either to the fact that exchange anisotropy is weak or to the fact that the variation of the bilinear-exchange parameter from one rare earth to another is similar to that of u_{2s}^0 . In any case the relative value of exchange anisotropy compared to the average value of exchange is probably not very important, since the variation of the average paramagnetic Curie temperature is not far from being proportional to $J(J+1)(g_J-1)^2$, which should be the case if the exchange is isotropic.²⁶

B. Determination of Two Kinds of Anisotropy from Susceptibility of Solid-Solution Single Crystals

In a random substitutional solid solution containing one kind of magnetic ion and one kind of nonmagnetic ion on the same crystallographic site A, there are cN magnetic ions and (1 - c)N nonmagnetic ions on A. If all the ions on the site A have the same valency, the crystalline potential on one magnetic ion is independent of c. When we perform the calculation of the paramagnetic magnetization as in Sec. IV, we obtain

$$\vec{\mathbf{M}} = \frac{cC}{T} \left(\vec{\mathbf{H}} - \frac{2J(J+1)}{c3NkT} \quad \vec{\mathbf{N}}_c \cdot \vec{\mathbf{H}} - \frac{(2J-1)(2J+3)}{10kT} \quad \vec{\mathbf{u}} \cdot \vec{\mathbf{H}} \right) + O\left(\frac{1}{T^3}\right), \quad (33)$$

where N is the Avogadro number and \overline{N}_c is the sum of the bilinear-exchange tensors associated with all the pairs of magnetic ions of the solid-solution single crystal.

In the following it is presumed that in the alloy under consideration the exchange interaction between two magnetic ions is independent of the other neighbors. This approximation may be used when the magnetic and nonmagnetic ions of the site Ahave almost the same size and the same chemical properties, and when the magnetic moments are well localized. The bilinear-exchange tensor \overline{n}_{ij} is only a function of the vector \mathbf{r}_{ij} joining two magnetic ions i and j and is independent of the position of the pair in the crystal. There are N pairs of atoms of the site A corresponding to a given $\vec{\mathbf{r}}_{ij}$: We can choose N origins, and since the sites A are identical, at the end of each vector $\mathbf{\tilde{r}}_{ii}$ there is another atom of the site A. Among the N origins, there are cN magnetic ions. If the magnetic ions have a perfectly random distribution without any segregation, among the cN vectors $\mathbf{\dot{r}}_{ii}$ whose origin is a magnetic ion, there are $c \times cN = c^2N$ vectors whose end is also a magnetic ion. There are $c^2 N$ pairs of magnetic ions for any value of $\vec{\mathbf{r}}_{ii}$. Then N_e is related to the tensor \overline{N} of the pure magnetic crystal (c=1) by

$$\overrightarrow{\mathbf{N}}_c = c^2 \overrightarrow{\mathbf{N}} \quad . \tag{34}$$

The explicit variation of the magnetization with concentration is given by

$$\vec{\mathbf{M}} = \frac{cC}{T} \left(\vec{\mathbf{H}} - c \, \frac{2J(J+1)}{3NkT} \, \vec{\mathbf{N}} \cdot \vec{\mathbf{H}} - \frac{(2J-1)(2J+3)}{10kT} \, \vec{\mathbf{u}} \cdot \vec{\mathbf{H}} \right) + O\left(\frac{1}{T^3}\right) \quad (35)$$

and the reciprocal susceptibility

$$\frac{1}{\chi} = \frac{1}{cC} \left(T + c \; \frac{2J(J+1)}{3Nk} \; \frac{\vec{\mathrm{H}} \cdot \vec{\mathrm{N}} \cdot \vec{\mathrm{H}}}{H^2} \right)$$

$$+\frac{(2J-1)(2J+3)}{10k} \frac{\vec{H} \cdot \vec{u} \cdot \vec{H}}{H^2} + O\left(\frac{1}{T}\right) . \quad (36)$$

The exchange contribution to the reciprocal susceptibility is constant, and the crystal field contribution is inversely proportional to the concentration.

The exchange anisotropy could then be distinguished from the single-ion anisotropy by the measurement of the paramagnetic susceptibility of single crystals of solid solutions with different concentrations of magnetic ions. One could distinguish the two anisotropies of rare-earth metals from the study of single crystals of alloys of rare earths with lanthanum, lutetium, and yttrium. This method should have the advantage over the method of Sec. VA of being perfectly rigorous and of needing less accuracy on the measurements of the paramagnetic susceptibility. The error due to the variation of the lattice parameters from one alloy to another should be smaller. Theoretically the average paramagnetic Curie temperature must be proportional to the concentration. The occurrence of segregation could be determined from the experimental variation of the average paramagnetic Curie temperature with the concentration.

VI. DIPOLAR MAGNETIC INTERACTIONS

In all the expressions above for the magnetization and susceptibility, the contribution of the dipolar interaction does not appear, because we had assimilated the dipolar Hamiltonian with a bilinearexchange term. Its contribution is included in the exchange tensor \overline{N} .

When J is a good quantum number, we can separate the tensor \overrightarrow{N} in a pure exchange tensor \overrightarrow{N}_{ex} and a dipolar tensor \overrightarrow{N}_{dip} with

$$\vec{\mathbf{N}}_{dip} = g_J^2 \mu_B^2 \sum_{(ij)i\neq j} \left(\frac{\vec{\mathbf{I}}}{r_{ij}^3} - \frac{3\vec{\mathbf{r}}_{ij} \times \vec{\mathbf{r}}_{ij}}{r_{ij}^5} \right) \quad , \tag{37}$$

where \vec{I} is the three-dimensional unit tensor and $\vec{r}_{ij} \times \vec{r}_{ij}$ the tensor product of the vector \vec{r}_{ij} by itself. The explicit contributions of the dipolar interactions to the magnetization and susceptibility are obtained by replacing \vec{N}_{dip} by its value given by Eq. (37).

When there is one kind of magnetic ion in one crystalline site, \overline{N}_{dip} is the product multiplied by $\frac{1}{2}N$ of the sum of the interactions of one magnetic ion with all the others, which can be calculated by the Lorentz method. The sum of the interactions between one atom and the atoms inside a small sphere centered on this atom is usually calculated numerically. The other atoms are assimilated in a classical distribution of magnetic moments which create the demagnetization field \overline{H}_{dc} . The contribution of \overline{H}_{de} to the magnetization \overline{M} is obtained in (25) by replacing \overline{H} by $\overline{H} + \overline{H}_{de}$. The dipolar interactions can be neglected for spherical rare-earth

single crystals, except for gadolinium, which is in an S state.

VII. FICTITIOUS SPIN

For many rare-earth insulators, the splitting of the fundamental J level of the free ion by the crystal field is much greater than kT even at relatively high temperatures. At room temperature or below, we cannot use the first terms of the expansion (10) of the magnetization with respect to 1/kTinside the J manifold because in this case this expansion converges much too slowly, as we shall see in Sec. VIIIB. When the magnetic ions are transition ions which are not in an S state (other than Fe³⁺ or Mn²⁺) the crystal field splitting is much bigger than the spin-orbit coupling and J is not a good quantum number. In all these cases, which represent many magnetic substances, we cannot use the exact expressions of the magnetization and susceptibility obtained in Sec. IV.

Very often these magnetic ions have a fundamental multiplet splitting much smaller than kT at the temperature where the measurements are performed, and the higher multiplets are at distances much greater than kT. In this case the energy levels are often represented as the eigenstates of a spin Hamiltonian expressed as a function of a fictitious spin \hat{S}' , whose components obey the commutation rules of the components of a real spin.^{27,28}

The most general spin Hamiltonian can be writ-

ten in the same way as a true Hamiltonian:

$$\begin{aligned} \mathcal{C} &= \sum_{\substack{(ij)i\neq j \ i \ (i) \ \mu \ (k)}} \sum_{\substack{(ij)i\neq j \ i \ (i) \ \mu \ (i)}} \sum_{\substack{(ij)i\neq j \ i \ (i) \ \mu \ (i)}} n_{ijl \ (i) \ \mu \ (i) \ l \ (j) \ \mu \ (j)} \\ &\times O_{I \ (i)}^{\mu \ (i)} \left(S'_{i}\right) O_{I \ (j)}^{\mu \ (j)} \left(S'_{j}\right) \\ &+ \sum_{k} \sum_{\substack{(k) \ \mu \ (k) \ \mu \ (k)}} u_{I \ (k)}^{\prime \mu \ (k)} O_{I \ (k)}^{\mu \ (k)} \left(\vec{S}'_{k}\right) - \sum_{k'} \vec{H} \cdot \vec{g} \cdot \vec{S}'_{k'} , \end{aligned}$$
(38)

when the dipolar term is assimilated to an exchange term. The coefficients $n'_{ij1(i)\mu(i)1(j)\mu(j)}$ and $u'^{\mu(k)}_{1(k)}$ are related both to the coefficients of real exchange and real crystal field by equations which can be very complicated. The Landé factor g_J is replaced by an anisotropic tensor \vec{g} . The time reversal does not necessarily reverse \vec{S}' . Then there are no selection rules on the parities of l_i , l_j , and l_k . The \vec{g} tensor is real and symmetrical and has at least three perpendicular axes of symmetry.

We have calculated the first terms of the magnetization in the same way as in Sec. IV. The coefficients $u'_{\alpha\beta}$ of the fictitious second-order crystal field have the same properties as the real second-order crystal field coefficients, since they are mathematical properties. In particular, $u'_{xx} + u'_{yy}$ $+ u'_{xx} = 0$. Generally, the tensors \overline{g} , $\overline{N'} = \sum_{\{i,j\} i \neq j} \overline{n'}_{ij}$, and $\overline{u'}$ have not the same symmetry axes. The magnetization is given by

$$\vec{\mathbf{M}} = \frac{\mathbf{c}'}{T} \left(\vec{\mathbf{g}} \cdot \vec{\mathbf{H}} - \frac{2S'(S'+1)}{3NkT} \quad \vec{\mathbf{g}} \cdot \vec{\mathbf{N}}' \cdot \vec{\mathbf{g}} \cdot \vec{\mathbf{H}} - \frac{(2S'-1)(2S'+3)}{10kT} \quad \vec{\mathbf{g}} \cdot \vec{\mathbf{u}}' \cdot \vec{\mathbf{g}} \cdot \vec{\mathbf{H}} \right) + O\left(\frac{1}{T^3}\right)$$
(39)

and the susceptibility is defined by $\chi = \vec{M} \cdot \vec{H} / H^2$, i.e.,

$$\frac{1}{\chi} = \frac{1}{e'} \frac{H^2}{\vec{\mathrm{H}} \cdot \vec{\mathrm{g}}^2 \cdot \vec{\mathrm{H}}} \left(T + \frac{2S'(S'+1)}{3Nk} \quad \frac{\vec{\mathrm{H}} \cdot \vec{\mathrm{g}} \cdot \vec{\mathrm{N}}' \cdot \vec{\mathrm{g}} \cdot \vec{\mathrm{H}}}{\vec{\mathrm{H}} \cdot \vec{\mathrm{g}}^2 \cdot \vec{\mathrm{H}}} + \frac{(2S'-1)(2S'+3)}{10k} \quad \frac{\vec{\mathrm{H}} \cdot \vec{\mathrm{g}} \cdot \vec{\mathrm{u}}' \cdot \vec{\mathrm{g}} \cdot \vec{\mathrm{H}}}{\vec{\mathrm{H}} \cdot \vec{\mathrm{g}}^2 \cdot \vec{\mathrm{H}}} \right) + O\left(\frac{1}{T}\right)$$

$$(40)$$

In these expressions,

$$\mathfrak{E}' = \frac{N\mu_B^2 S'(S'+1)}{3k}$$

is the part of the Curie constant independent of \overline{g} . They are very similar to the expressions inside the J manifold. Though there are no selection rules on the parities of l_i , l_j , and l_k , there are the same selection rules on the magnetization and reciprocal susceptibilities at the above orders in 1/Tas before. The magnetization to second-order in 1/T and the reciprocal susceptibility to zeroth order in 1/T are dependent only on the fictitious bilinear exchange and on the fictitious second-order crystal field. But these coefficients may be dependent on various order coefficients of real exchange and real crystal field.

When the crystal has at least three perpendicular axes of symmetry \bar{x} , \bar{y} , \bar{z} , along one axis of symmetry \bar{z} we have

$$\frac{1}{\chi_{z}} = \frac{1}{g_{zz}^{2} c'} \left(1 + \frac{2S'(S'+1)}{3Nk} N'_{zz} + \frac{(2S'-1)(2S'+3)}{10k} u'_{zz} \right) + O\left(\frac{1}{T}\right) . \quad (41)$$

VIII. SUSCEPTIBILITY TO THIRD ORDER IN RECIPROCAL TEMPERATURE

A. Expression for Susceptibility

From Eq. (3) we deduce that the third-order term of the magnetization along an axis \overline{z} is

$$M_{z,3} = \frac{1}{(2J+1)^{N} k^{3} T^{3}} \times \left(\frac{\sum_{h} \left[\partial(W_{h}^{4}) / \partial H_{z} \right]}{24} \cdot \frac{(\sum_{h} W_{h}^{2}) \left\{ \sum_{h'} \left[\partial(W_{h'}^{2}) / \partial H_{z} \right] \right\}}{4(2J+1)^{N}} \right).$$
(42)

There is no selection rule for the contribution of the different exchange terms to the third-order term. Since the general expression of this term should be very complicated, we have calculated the third-order term only in the case of a bilinear exchange and for a crystal with at least three axes of symmetry \mathbf{x} , \mathbf{y} , \mathbf{z} of arbitrary order.

The calculation of the third-order term is similar to the calculation of the preceding terms; it is done using the relations given in Sec. III. It is available on request.

The susceptibility along the \dot{z} axis, $\chi_z = M_z / H_z$, is given by

$$\chi_{z} = \frac{C}{T} \left\{ 1 - \frac{2J(J+1)}{3NkT} N_{zz} - \frac{(2J-1)(2J+3)}{5kT} u_{2z}^{0} + \frac{1}{k^{2}T^{2}} \left[\frac{4J^{2}(J+1)^{2}}{9N^{2}} N_{zz}^{2} + \frac{4}{15} J(J+1)(2J-1)(2J+3) \frac{u_{2z}^{0}}{N} N_{zz} + \frac{2\mathrm{Tr}_{10}(V^{2}J_{z}^{2}) + \mathrm{Tr}_{10}(VJ_{z}VJ_{z})}{2J(J+1)(2J+1)} - \frac{\mathrm{Tr}_{10}(V^{2})}{2(2J+1)} - \frac{J(J+1)}{45N} (2J^{2}+2J+1) \sum_{(ij)i \neq j} \left(2\sum_{\alpha} n_{ijz\alpha}^{2} + \sum_{\alpha\beta} n_{ij\alpha\beta}^{2} \right) - \frac{2J^{2}+2J+1}{30} g_{J}^{2} \mu_{B}^{2} H^{2} \right\} + O\left(\frac{1}{T^{4}}\right)$$
(43)

and the susceptibilities along \mathbf{x} and \mathbf{y} are obtained by replacing in the expression of χ_{z} the index z, by x and y, respectively. Since χ_x , χ_y , and χ_z are independent of the direction of the magnetic field to this order in 1/T, the susceptibility $\chi = \vec{M} \cdot \vec{H}/$ H^2 given by

$$\chi = \chi_x \alpha_H^2 + \chi_y \beta_H^2 + \chi_z \gamma_H^2$$

varies as the squares of the direction cosines of the magnetic field.

The reciprocal susceptibility along the \dot{z} axis is given by

$$\frac{1}{\chi_{z}} = \frac{1}{C} \left\{ T + \frac{2J(J+1)}{3Nk} N_{zz} + \frac{(2J-1)(2J+3)}{5k} u_{2z}^{0} + \frac{1}{k^{2}T} \left[\frac{(2J-1)^{2}(2J+3)^{2}}{25} u_{2z}^{02} - \frac{2\mathrm{Tr}_{io}(V^{2}J_{z}^{2}) + \mathrm{Tr}_{io}(VJ_{z}VJ_{z})}{2J(J+1)(2J+1)} + \frac{\mathrm{Tr}_{io}(V^{2})}{2(2J+1)} + \frac{J(J+1)(2J^{2}+2J+1)}{45N} \sum_{(ij)_{i\neq j}} \left(2\sum_{\alpha} n_{ijz\alpha}^{2} + \sum_{\alpha\beta} n_{ij\alpha\beta}^{2} \right) + \frac{2J^{2}+2J+1}{30} g_{J}^{2} \mu_{B}^{2} H^{2} \right\} + O\left(\frac{1}{T^{2}}\right) .$$
(44)

The contributions of the exchange and the crystalline potential to the paramagnetic Curie temperature $\theta_{pz} = \theta_{pex,z} + \theta_{pv,z}$ along the \bar{z} axis are

$$\begin{aligned} \theta_{pex,z} &= -\frac{2J(J+1)}{3Nk} \ N_{zz} \\ d \\ \theta_{pv,z} &= -\frac{(2J-1)(2J+3)}{5k} \ u_{2z}^{0} \ . \end{aligned}$$

and

There are contributions of
$$\theta_{pex,z}^2$$
, $\theta_{pex,z}$, $\theta_{pv,z}$, $\theta_{pv,z}^2$, $\theta_{pv,z}^2$, to the term in $1/T^3$ of χ_z and in $1/T$ of $1/\chi_z$. They bring no new information compared to the terms of lower order. It could be predicted that these terms should appear either in χ_z or in $1/\chi_z$ by comparison of the expansions of χ_z and $1/\chi_z$; they can be considered as "parasitic terms." They are the same as in the molecular-field approximation.¹¹

We remark that the nonparasitic coefficient of $1/k^2 T$ in expression (44) for $1/\chi_z$ is just the opposite of that of $1/k^2T^2$ in expression (43) for χ_z .

The contribution of the crystal field to the susceptibility in third order in the reciprocal tempera-

ture appears in $\operatorname{Tr}_{io}(V^2 J_z^2)$, $\operatorname{Tr}_{io}(V J_z V J_z)$, $\operatorname{Tr}_{io}(V^2)$. This contribution is the same as in the molecularfield approximation.¹¹ It is not necessary to give a general explicit expression of $\operatorname{Tr}_{io}(V^2 J_z^2)$ and $\operatorname{Tr}_{io}(VJ_{z}VJ_{z})$ as functions of the coefficients of the crystal field. In each particular case we obtain explicit expressions from the traces of products of components of \overline{J} .¹⁷ The expression for the third term is

$$\operatorname{Tr}_{io}(V^2) = \sum_{l,\mu} (u_l^{\mu})^2 \operatorname{Tr}_{io} [O_l^{\mu} (\hat{\mathbf{J}})^2].$$

The summation

(

$$\sum_{ij)i \neq j} \left(2 \sum_{\alpha} n_{ijz\alpha}^2 + \sum_{\alpha\beta} n_{ij\alpha\beta}^2 \right) ,$$

which can also be written

$$\sum_{(ij)i \neq j} \left[3n_{ijzz}^2 + 4(n_{ijzx}^2 + n_{ijzy}^2) + n_{ijxx}^2 + n_{ijyy}^2 + 2n_{ijxy}^2 \right],$$

represents the contribution of the exchange to the reciprocal susceptibility in the 1/T term. This contribution does not exist in the molecular-field

approximation.¹¹ It corresponds to the first deviation from the Curie-Weiss law for the initial reciprocal susceptibility of an isotropic single crystal.

The last term is proportional to H^2 . It is the first saturation term. It is different from the first saturation term obtained in the molecular-field approximation,¹¹ where H^2 is replaced by H^2_{eff} , \bar{H}_{eff} being the effective field which is the sum of the applied magnetic field and the molecular field.

Thus we see that one of the reasons for calculating the third-order term of the susceptibility is to find deviations from the molecular-field approximation.

B. Relative Magnitudes of $1/T^3$ Term and 1/T Term in Series Expansions of χ and $1/\chi$, Respectively

 $\theta_{pex,z}$ is of the order of magnitude of the average paramagnetic Curie temperature θ_{pm} . Very roughly, $k\theta_{pv,z}$ is of the order of magnitude of the splitting of the *J* level by the crystal field. The nonparasitic contribution of the crystalline potential to the coefficient of $1/k^2CT$ in the reciprocal susceptibility is of the same order of magnitude as the parasitic contribution. When the exchange is isotropic the nonparasitic contribution of exchange to the coefficient of $1/k^2CT$ is of the order of magnitude of

$$\frac{J^4}{N} \sum_{(ij)i\neq j} n_{ij}^2$$

$$J^{4}\Sigma$$

or

$$J^{4}\sum_{i\neq 1}n_{1i}^{2}$$
.

The parasitic contribution is of the order of magnitude of

$$J^{4}\left(\sum_{i\neq 1}n_{1i}\right)^{2} = J^{4}\left(\sum_{i\neq 1}n_{1i}^{2} + \sum_{j\neq 1, k\neq 1}n_{1j}n_{1k}\right)$$

When there are long-range exchange interactions, the contribution of the off-diagonal terms will be very important, and the nonparasitic contribution will be small compared to the parasitic contribution of the exchange. This could be predicted, since in this case the molecular field is a good approximation. When there are short-range exchange interactions, the two contributions will be of the same order of magnitude.

Then in every case the $1/T^3$ term in the series expansion for χ is of the order of magnitude of its parasitic terms. When the exchange is more important than the crystalline potential $(\theta_{pex,z} > \theta_{pv,z})$, the ratio of the $1/T^3$ term to the $1/T^2$ term is of the order of θ_{pm}/T . The $1/T^3$ term can be neglected only at temperatures much higher than θ_{pm} , for which $\theta_{pm}/T \ll 1$.

In the first-order term of the expansion of $1/\chi_z$, the parasitic term $\theta_{pv,z}^2/T$ and the nonparasitic

contribution of the crystal field are comparable, and the contribution of exchange will be generally smaller than or of the same order of magnitude as the two other terms except when there are important short-range exchange interactions. Then the first-order term will be small compared to the zero-order term when the splitting of the fundamental J level is smaller than kT. This is equivalent to the condition that T is larger than the anisotropy of the paramagnetic Curie temperature. T must also be not too close to the ordering temperature. Roughly, these conditions are fulfilled when the relative anisotropy of the susceptibility is smaller than 1. For rare-earth single crystals they are satisfied from a temperature of about 50° above the ordering temperature.

When the exchange energy is more important than the anisotropy energy, or when the relative anisotropy of the paramagnetic Curie temperature is smaller than 1 (case of rare-earth metals), it is better to use the two first terms of the reciprocal susceptibility than those of the susceptibility.

The contribution of the term proportional to H^2 to the first-order term in the expansion of $1/\chi$ is comparable to the other parts of the first-order term for a magnetic field of the order of 10^5 Oe when the anisotropy of the paramagnetic Curie temperature is of the order of 10 K. Then, for the usual magnetic fields, the convergence of χ and of $1/\chi$ are almost the same as the convergence of the initial χ and $1/\chi$, respectively, except when we are a few degrees above the ordering temperature.

C. Rare-Earth Metals

In the case of rare-earth metals the first-order term of the expansion of $1/\chi$ can be observed in accurate measurements between the ordering temperature and room temperature. In the analysis of the data, one must take care of the variation of the paramagnetic susceptibility due to the variation of the lattice parameters with the temperature. Since the convergence of the expansion is not known accurately, it is necessary to check carefully whether the measured term does vary as 1/T.

In gadolinium, we can neglect the anisotropy. From the 1/T term of $1/\chi$ we can deduce the quantity $\sum_{(ij)i\neq j} n_{ij}^2$. The knowledge of $\sum_{(ij)i\neq j} n_{ij}$ and $\sum_{(ij)i\neq j} n_{ij}^2$ could give some new information on the variation of the exchange interactions with interatomic distances. In other rare earths, the 1/T term could give us some information about exchange and single-ion anisotropy.

IX. SECOND SATURATION TERM

The fourth-order term of the 1/T expansion of χ contains a constant term and a term which is quadratic in the magnetic field. The latter is the second saturation term, which depends both on the

intensity and the direction of the magnetic field. By calculating this term, we have found that it has two interesting properties: It depends only on the second- and fourth-order crystal field parameters and on bilinear and biquadratic exchange, and it is not too small to be measured.

From Eq. (3) we obtain the fourth-order term of the magnetization along the \vec{z} axis:

$$M_{z,4} = \frac{1}{(2J+1)^{N} k^{4} T^{4}} \left(\frac{\sum_{h} (\partial W_{h}^{5} / \partial H_{z})}{120} + \frac{\sum_{h} W_{h}^{2} \sum_{h'} (\partial W_{h'}^{3} / \partial H_{z})}{12(2J+1)^{N}} + \frac{\sum_{h} W_{h}^{3} \sum_{h'} (\partial W_{h'}^{2} / \partial H_{z})}{12(2J+1)^{N}} \right)$$
(45)

The term $\sum_{h} W_{h}^{2}$ and the part of $\sum_{h} W_{h}^{3}$ which is dependent of \overline{H} give contributions to the second saturation term, which depends only on the second-order crystal field and on bilinear exchange. The term $\sum_{h} W_{h}^{5} = \operatorname{Tr}(\mathcal{H}^{5})$ contributes to the second saturation term by

$$\sum_{\text{erm}} \mathbf{Tr}_{cr} (\mathcal{H}_{ex} \mathcal{H}_{z}^{4}) = 5 \mathbf{Tr}_{cr} (\mathcal{H}_{ex} \mathcal{H}_{z}^{4})$$

and

$$\sum_{\text{perm}} \operatorname{Tr}_{cr} (V\mathcal{K}_{Z}^{4}) = 5 \operatorname{Tr}_{cr} (V\mathcal{K}_{Z}^{4}) \cdot \operatorname{Tr}_{cr} (V\mathcal{K}_{Z}^{4})$$
$$= g_{J}^{4} \mu_{B}^{4} \sum_{i_{1}i_{2}i_{3}i_{4}i_{5}} \sum_{i_{\mu}} u_{i_{\mu}}$$
$$\times \operatorname{Tr}_{cr} [O_{i}^{\mu} (\mathbf{J}_{i_{1}}) (\mathbf{J}_{i_{2}} \cdot \mathbf{H}) (\mathbf{J}_{i_{3}} \cdot \mathbf{H})$$
$$\times (\mathbf{J}_{i_{4}} \cdot \mathbf{H}) (\mathbf{J}_{i_{5}} \cdot \mathbf{H})].$$

The nonzero traces of this sum correspond to two cases. In the first case, two indices are equal to i_1 and the two other are equal to each other. It gives a contribution which depends only on the second-order crystal field. In the second case, all the indices are equal. Each term of $(\bar{J} \cdot \bar{H})^4$ transforms in a rotation as $\mathfrak{D}_1 \times \mathfrak{D}_1 \times \mathfrak{D}_1 \times \mathfrak{D}_1 \times \mathfrak{D}_1$ which contains \mathfrak{D}_0 , \mathfrak{D}_1 , \mathfrak{D}_2 , \mathfrak{D}_3 , \mathfrak{D}_4 . Since the trace must transform as \mathfrak{D}_0 , it is nonzero only if l=2 or 4. We have thus demonstrated that the second saturation term is dependent only on the second- and fourth-order crystal field.

The expression of $\operatorname{Tr}_{\operatorname{cr}}(\mathscr{H}_{\operatorname{ex}}\mathscr{H}_Z^4)$ is

$$\operatorname{Tr}_{\mathrm{cr}}(\mathscr{H}_{\mathrm{ex}}\mathscr{H}_{Z}^{4}) = g_{J}^{4} \mu_{B}^{4} \sum_{(ij)i \neq j} \sum_{\substack{i(i) \mid \mu(i) \\ (ij) \mid i \neq j}} \sum_{\substack{i(i) \mid \mu(i) \\ (i) \mid \mu(i) \\ (i) \mid \mu(j) \\ (i)$$

Since $(\mathbf{\tilde{J}}_{k1} \cdot \mathbf{\tilde{H}}) (\mathbf{\tilde{J}}_{k2} \cdot \mathbf{\tilde{H}}) (\mathbf{\tilde{J}}_{k3} \cdot \mathbf{\tilde{H}}) (\mathbf{\tilde{J}}_{k4} \cdot \mathbf{\tilde{H}})$ contains only terms varying as \mathfrak{D}_0 , \mathfrak{D}_1 , \mathfrak{D}_2 , \mathfrak{D}_3 , \mathfrak{D}_4 , the representation \mathfrak{D}_4 being present for $k_1 = k_2 = k_3 = k_4$, $l(i) \leq 4$ and $l(j) \leq 4$. In order that a trace be other than zero when l(i) = 4, it is necessary that all the k's should be equal to *i*. In this case, however, $\mathbf{Tr} [O_l^{\mu} \binom{U}{2} (\mathbf{\tilde{J}})] = 0$ should be isolated, and then all the traces are zero. Then $l(i) \leq 3$ and $l(j) \leq 3$. If l(i)

= 3, the trace is nonzero only if 3 k are equal to i and the other equal to j. In this case l(j)=1. If l(i)=2, l(j)=2, since $0 < l(j) \le 3$ and l(j) is of the same parity as l(i). The possible cases are l(i)=l(j)=1, l(i)=1, l(j)=3 or l(i)=3, l(j)=1, and l(i)=l(j)=2. We have demonstrated that the second saturation term is dependent only on a bilinear and biquadratic exchange.

We have calculated the second saturation term in the case where there is only a second-order crystalline potential and a bilinear exchange, and where the crystal has at least three axes of symmetry of order at least two. The contribution of this term to the susceptibility along a symmetry axis is

$$\chi_{zs,4} = \frac{C}{T} \frac{1}{k^3 T^3} \left(\frac{2}{45N} J(J+1) \left(2J^2 + 2J + 1 \right) g_J^2 \mu_B^2 \right) \\ \times \left[N_{xx} H_x^2 + N_{yy} H_y^2 + N_{zz} (H_z^2 + H^2) \right] + \frac{(2J-1) (2J+3)}{420} \\ \times (8J^2 + 8J + 5) g_J^2 \mu_B^2 \left[u_{2x}^0 H_x^2 + u_{2y}^0 H_y^2 + u_{2z}^0 (H_z^2 + H^2) \right] \right).$$
(46)

In the following $b = (2J^2 + 2J + 1/30k^2)g_J^2\mu_B^2$ is the coefficient of the first saturation term in the expression of $1/\chi_z$ and $c_{2z}(\vec{H})$ is the coefficient of $(C/T)(1/T^3)$ in $\chi_{zs,4}$. The second saturation term of the reciprocal susceptibility is

$$\left(\frac{1}{\chi_z}\right)_{s,2} = \frac{1}{CT^2} \left[-2\theta_{pz} b H^2 - c_{2z}(\vec{H}) \right], \qquad (47)$$

whose explicit expression is

$$\frac{\left(\frac{1}{\chi_{z}}\right)_{s,2}}{(1+1)} = \frac{1}{Ck^{3}T^{2}} \left(-\frac{2}{45N} J(J+1) \left(2J^{2}+2J+1\right)g^{2}_{J}\mu_{B}^{2}\right) \\ \times \left(N_{xx}H^{2}_{x}+N_{yy}H^{2}_{y}+N_{zz}H^{2}_{z}\right) + \frac{\left(2J-1\right)\left(2J+3\right)}{2100} \\ \times \left(16J^{2}+16J+3\right)g^{2}_{J}\mu_{B}^{2}u_{2z}^{0}H^{2} - \frac{\left(2J-1\right)\left(2J+3\right)}{420} \\ \times \left(8J^{2}+8J+5\right)\left(u_{2x}^{0}H^{2}_{x}+u_{2y}^{0}H^{2}_{y}+u_{2z}^{0}H^{2}_{z}\right)\right).$$
(48)

In the expressions (46) and (47) we cannot distinguish clearly between parasitic and nonparasitic terms. The term $c_{2z}(\vec{H})$ is of the same order of magnitude as $2\theta_{pz}bH^2$. The ratio of the second saturation term to the first saturation term is then of the order of magnitude of

$$\frac{2\theta_{pz}bH^2}{CT^2} \frac{TC}{bH^2} = \frac{2\theta_{pz}}{T}$$

For rare-earth metals at room temperature the two saturation terms are of the same order of magnitude. Then the second saturation term can be measured, as well as the first, in magnetic fields of the order of 100 kOe.¹⁴ In this way it should be possible to obtain new information on exchange and single-ion anisotropy if very accurate measurements are available. The effect of magnetostriction must be carefully evaluated.²⁴

X. CONCLUSION

The expression of the susceptibility obtained by this general method should be very useful for the study of rare-earth-metal single crystals. Using the two selection rules for the constant term of the reciprocal susceptibility, one can distinguish between single-ion and two-ion anisotropy. The term in 1/T and the second saturation term can give other useful information.

More generally, the expressions for the susceptibility obtained here can be useful when the splitting of the fundamental J level is smaller or of the order of kT and the first excited level is much higher than kT, or when there is a fundamental multiplet described by a fictitious spin, whose distance to the first excited level is much higher than kT. These expressions are not valid at temperatures close to the ordering point.

This calculation can be used for the following substances when one kind of magnetic ion is on equivalent crystalline sites. In single crystals of rare-earth metals or of ordered or disordered compounds of rare-earth metals with nonmagnetic metals, the exchange and the crystal field interactions are generally important, and the splitting of the fundamental J level is generally smaller than kT above the ordering temperature. The method of studying the compounds is analogous to that to be used for the pure rare-earth metals.

Among the rare-earth insulators, there are substances in which the splitting of the fundamental J level is greater than kT at room temperature (as rare-earth hydroxides or rare-earth chlorides), and others in which the splitting of the fundamental J level is on the order of kT or smaller than kTat room temperature (example: rare-earth oxy-

sulfides). In the first case, the exact expressions for the first few terms of the susceptibility can be used for determining the exchange parameters for gadolinium which is in an S state, and it can be used with a fictitious spin for other rare earths. $^{7-10}$ In the second case, the exact expressions for the first few terms of the susceptibility expressed in terms of the parameters of the real Hamiltonian can be used for all the rare earths. But the exchange interactions are generally small and thus the ordering temperatures are weak compared to the splitting of the J level. Typical examples are the rare-earth oxysulfides. For these substances the ordering temperatures, when they exist, are on the order of a few degrees kelvin.²⁹ The expansion of the susceptibility can be used at room temperature. From the constant term of the reciprocal susceptibility we can deduce u_2^0 immediately. But since the exchange is small, the exact expression for the initial susceptibility has no advantage compared to the molecular-field approximation. Although it requires the use of a computer, the Van Vleck method^{30,31} is more advantageous because it can give approximate values of all the crystal field parameters.^{32,33} But in this case the measurement of the second saturation term could be very useful, because it should give the fourthorder crystal field parameter without a computer, and could be used to check the results coming from the Van Vleck method or from the spectroscopic measurements.

The exact expression for the leading terms of the susceptibility can be used for the determination of exchange parameters in insulators containing Fe³⁺ or Mn^{2*} , which are in an S state, as has been done for $Gd(OH)_3$. For other compounds containing transition ions, the exact expression for the leading terms of the susceptibility can yield new information only when a fictitious spin can be used.

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Elastic Properties of DySb near the Magnetic and Structural Phase Transition

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The shear elastic constants $c_{\theta} = (c_{11} - c_{12})/2$ and c_{44} have been measured in DySb. c_{44} shows a small softening of about 0.6% at the phase transition, while $c_{\theta} = (c_{11} - c_{12})/2$ exhibits a 58% drop. The large change in $c_{\theta} = (c_{11} - c_{12})/2$ occurs over a temperature range of more than 200 K. The dominant mechanism for the softening of the elastic constant $c_{\theta} = (c_{11} - c_{12})/2$ is a Jahn-Teller strain coupling. Strong-biquadratic pair interactions are present which compete with the strain coupling.

There has been much interest recently in the magnetic and structural phase transition in DySb. $^{\rm 1-3}$ The system was originally thought to undergo successive magnetic and structural transitions at 9.5 and 11.5 °K, respectively. However, a recent study of the magnetic properties³ revealed a single first-order magnetic and structural phase transition which occurred at 9.5°K. This work left unresolved the question of the microscopic origin of the transition. As was suggested, soundvelocity measurements should help to resolve this point. In this paper (i) we report the results of the first measurement of the shear elastic constants $c_{\theta} = \frac{1}{2} (c_{11} - c_{12})$ and c_{44} through the phase transition⁴ and (ii) we present the results of our fit to the elastic constant c_{θ} .

We find that the $E_{g}^{\theta}(\Gamma_{31}^{*})$ strain coupling to the dysprosium ions is the dominant mechanism for the softening of the elastic constant c_{g} . By itself,

this coupling would produce a cooperative firstorder Jahn-Teller phase transition at about 6 °K. However, the elastic constant c_{θ} does not continue to soften past 9.5 °K because the exchange interactions present in DySb cause the system to undergo a first-order phase transition at 9.5 °K.

We studied two samples⁵ of DySb, both of which were originally rectangular in shape, with the sides being normal to [100] axes. The corners of each sample were polished flat to obtain faces normal to the [110] axis, with the resulting faces being approximately 1.5 mm on a side. Sample I was 2.1 mm in length, while sample II was 1.8 mm. The sound-velocity changes were measured using a pulse-echo phase-comparison technique which is described in detail elsewhere.⁶

In Fig. 1 we show the change in the elastic constant c_{θ} as function of temperature from 3.5 to 360 °K for sample I. Sample II gave essentially