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# Location of Gadolinium Ions in Hydrated Oxalate by ESR

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Gadolinium oxalate hydrate crystallizes isomorphously as $La_2(C_2O_4)_3 \cdot 10H_2O$, with two molecules in a unit cell of dimensions: $a_0=11.61+0.05$, $b_0=9.656+0.020$, $c_0=10.22+0.05$ Å and $\beta=119.0+0.1°$. A detailed study of the *d*-spacings for the coprecipitates of varying composition in the La-Gd oxalate system was made, and 46 nearest-neighbor pairs were selected for Van Vleck second moment calculation. Agreement of the results of the calculation with those of the experiment justifies the suggested model representing the location of the gadolinium ions in the hydrated oxalate salt.

During the course of investigation of the coprecipitated phases of calcium-gadolinium oxalate system[1] the author found it desirable to know the relative positions of gadolinium ions in the lattice of the hydrated salt. However, no such information is available in literature. In the work of Gilpin and

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[1] H. Chi and K. Nagashima, This Bulletin, **41**, 2054 (1968).

McCrone[2,3] concerning the crystallographic data of hydrated lanthanum oxalate, the authors did not seem to pay attention to the structural refinements or to the location of ions in such a specified lattice. Studies on the single crystal X-ray data of oxalates of rare-earths other than lanthanum cannot be carried out easily. This is because most of these salts, prepared from their aqueous solutions, can be obtained only in the form of a fine powder.

In this article a new result is presented. Even when direct crystallographic data are lacking or a well-resolved Fourier projection has not been examined, recent refinements of ESR measurements enable one to obtain detailed information for the distribution of paramagnetic ions in solids.[4,5] In favorable cases, we can solve problems concerning the exact location of each kind of paramagnetic ions in their respective crystals.

Since the gadolinium ion has no resultant orbital momentum, it is very active to ESR at room temperature.[6] The author has therefore worked on the following presumption: ESR may offer excellent opportunities of providing exact knowledge of the location of lanthanide ions in crystals. The only necessary condition is that they are similarly located to gadolinium ions in their respective crystals. Thus, gadolinium ions may be regarded as a guide in ESR experiments for determining the exact positions of other allied lanthanide ions, either less active to ESR or perfectly inert, in many kinds of isomorphous salts.

The Van Vleck calculation of the magnetic second moment for a polycrystalline sample usually gives good results which are valuable for the verification of ESR experimental data.[7] However, in order to use the Van Vleck equation for this purpose, we need a fixed model in which the distances between the nearest neighboring paramagnetic ions are precisely known. In the present study, the process is reversed. The Van Vleck calculation is used as an independent means to determine whether or not the positions of the paramagnetic ions are crystallographically well fitted.

## Experimental

**Reagents and Procedure.** Lanthanum oxide was dissolved in nitric acid and heated on a water bath until crystallization took place. The resulting lanthanum nitrate was dissolved and diluted. Gadolinium oxide was treated in the same way. The two solutions were then mixed in various proportions. A total of 200 m*l* each of the resulting solutions contained 1.25 mM of tripositive ions. The pH value of the solutions was adjusted to near 1.5. Three series of the specimens were prepared. To each of them was added 50 m*l* of water containing 1 g of oxalic acid or dimethyl oxalate, the latter being used to effect homogeneous precipitation. In the first series, oxalic acid was added as a precipitant at room temperature. In the second, dimethyl oxalate was added at room temperature. In the last, dimethyl oxalate was added and the temperature was held at about 80°C. In the first instance, the mixtures turned turbid at once. However, in the case of homogeneous precipitation, the reaction proceeded very slowly and lasted from 8 to 16 hr. Generally, the smaller the content of gadolinium in the solution, the slower was the rate of precipitation. All the precipitates were allowed to settle overnight, filtered, washed and air-dried. One part from each of the precipitates was taken for X-ray powder study, and the remaining was used for ESR spectrometry.

**Apparatus.** Measurement for electron spin resonance was carried out at room temperature swept both increasingly from 250 up to 10000 gauss and decreasingly from 10000 down to 250 gauss with a JES-3BS-X ESR spectrometer, manufactured by the Japan Electron Optics Laboratory. The X-ray measurement was carried out with a Rigaku-Denki X-ray diffractometer operated at 30 KV and 15 mA, using a copper target.

## Results and Discussion

**A. X-Ray Diffractometry.** The author studied carefully the *d*-spacings for each of the coprecipitates of varying composition in the lanthanum-gadolinium oxalate system. The coprecipitates were prepared by three different procedures. It was observed that in each case the *d*-spacings, except for $d_{020}$, changed slightly and regularly with composition. Three typical and strong diffraction data together with the corresponding axial lengths were selected. They are listed in Table 1 for comparison.

In Table 1, the values of each of the cell dimensions were calculated from the general relation: Monoclinic: $a : 1 : c$, $\alpha = \gamma = 90°$, $\beta \neq 90°$

Table 1. Shrinkage along $a$ and $c$ axes of lanthanum oxalate decahydrate

| Spacing and Axis | Alteration of the lattice of Hydrated La-Gd Oxalate (Å) Mole Fraction of Gadolinium | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 0.20 | 0.40 | 0.60 | 0.80 | 1.00 |
| (1) $d_{100}$ | 10.40 | 10.36 | 10.30 | 10.25 | 10.20 | 10.16 |
| $a_0$ | 11.91 | 11.86 | 11.78 | 11.72 | 11.66 | 11.61 |
| (2) $d_{011}$ | 6.66 | 6.63 | 6.60 | 6.58 | 6.57 | 6.56 |
| $c_0$ | 10.47 | 10.41 | 10.35 | 10.30 | 10.26 | 10.22 |
| (3) $d_{020}$ | 4.84 | 4.84 | 4.84 | 4.84 | 4.83 | 4.83 |
| $b_0$ | 9.68 | 9.68 | 9.68 | 9.68 | 9.66 | 9.66 |

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[2] V. Gilpin and W. C. McCrone, *Anal. Chem.*, **24**, 225 (1952).

[3] Fink, Inorganic Index to the Powder Diffraction File, **14**, 775, ASTM Publication (1965).

[4] S. Fujiwara, *Anal. Chem.*, **36**, 2259 (1964).

[5] S. Fujiwara and K. Nagashima, *ibid.*, **38**, 1464 (1967).

[6] F. W. Lancaster and W. Gordy, *J. Chem. Phys.*, **19**, 1181 (1951).

[7] G. E. Pake and E. M. Purcell, *Phys. Rev.*, **74**, 1184 (1948).

$$d_{hkl} = \frac{b_0}{\sqrt{\dfrac{(h/a)^2 + (l/c)^2 - \dfrac{2hl}{ac}\cos\beta}{\sin^2\beta} + k^2}} \qquad (1)$$

where $a = a_0/b_0$, $c = c_0/b_0$.

The results indicate that with the replacement of lanthanum ions by smaller gadolinium ions, the angle $\beta$ remains unchanged in all cases, and most of the shrinkage occurs along $a$ and $c$ axes in the proportion of 1 : 0.88 which is approximately equal to the axial ratio of pure lanthanum oxalate decahydrate. Although $a_0$ and $c_0$ in this coprecipitated system vary linearly with the mole fraction of gadolinium, the shortest $b$-axis only shows little variation to the extent of 0.02 Å with change of composition.

In order to ascertain whether the mole number of hydration was altered the author analyzed both the pure precipitates and the coprecipitates. All gave the same result, with the mole number lying around 10. Analysis of pure lanthanum oxalate and pure gadolinium oxalate precipitated by the three procedures described above, gave the average mole number as 10.58 and 10.49, respectively. The calculated density of the latter 2.514 g/cm$^3$ for the two formula weights in a unit cell agreed with that obtained (2.49$\pm$0.01 g/cm$^3$ at 28°) by means of flotation and pyconometry.

**B. Validity of the Van Vleck Equation.** The Van Vleck equation in a general form[8] is expressed as

$$\langle \Delta\nu^2 \rangle = \frac{3}{4} g^4 \mu_B{}^4 h^{-2} s(s+1) \sum_j r_{jk}^{-6} (3\cos^2\theta - 1)^2 \qquad (2)$$

Under the present experimental conditions of varying external magnetic field for a fixed frequency, an equivalent magnetic field second moment $\langle \Delta H^2 \rangle$ is conveniently computed instead of $\langle \Delta\nu^2 \rangle$ for very fine polycrystalline specimens, like those used in this experiment, the powers of the direction cosines can be replaced by their average over a sphere. Neglecting surface effect, equation (2) may be transformed into a precise and useful equation as

$$\langle \Delta H^2 \rangle_{\rm calc} = \frac{3}{5} g^2 \mu_B{}^2 s(s+1) \sum_j r_{jk}^{-6} \qquad (3)$$

The theoretical values can be readily calculated by means of (3) on the basis of X-ray diffraction data. For the present purpose, $g$ is taken to be 2.0023 and $s$ to be 7/2 for free Gd$^{3+}$. The Bohr magneton $\mu_B$ has its usual value $9.2732 \times 10^{-21}$ erg/gauss. The Van Vleck equation may be rewritten for this special case in a very simple form:

$$\langle \Delta H^2 \rangle_{\rm calc} = 3.258 \times 10^9 \sum_j r_{jk}^{-6} \qquad (4)$$

In this equation $r$ and $\langle \Delta H^2 \rangle_{\rm calc}$ are given in Ångstroms and gauss$^2$ respectively.

We come now to the point in question: How will gadolinium ions orient themselves so as to provide a proper summation term as shown in Eq. (4). In this summation term, every $r$-value must satisfy theoretically probable conditions; the total amount of the negative sixth power of every $r$-value must also give a correct answer for the $\langle \Delta H^2 \rangle_{\rm calc}$ in coincidence with the result obtained from the ESR measurements.

The theoretically probable conditions are not restricted to the verification based on $d$-spacing data. The following aspects have also been noted.

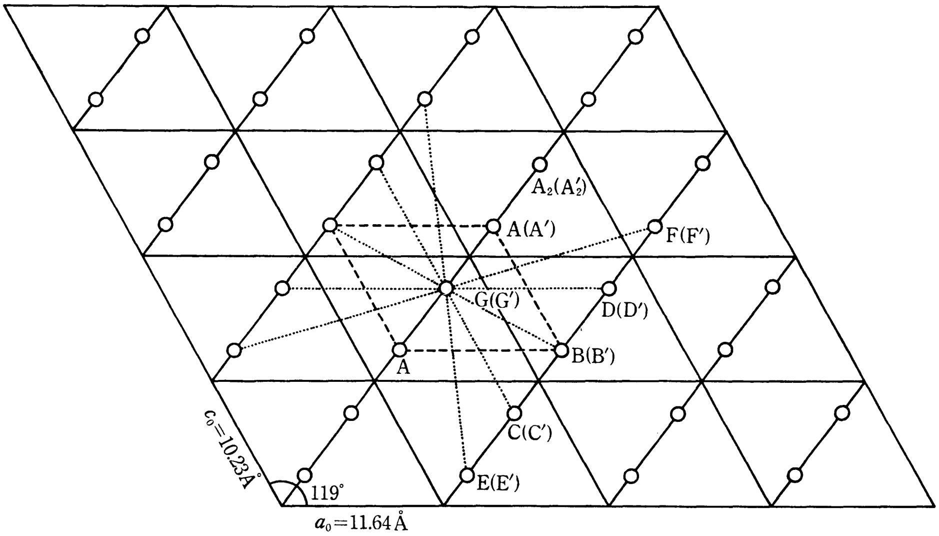

Fig. 1. Location of Gadolinium Ions on the a—c Plane.

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[8] J. H. Van Vleck, *Phys. Rev.*, **74**, 1168 (1948).

Table 2. Distances assumed for the nearest neighboring gadolinium ion in the lattice of hydrated oxalate

| $r$-Value* | | | | |
|---|---|---|---|---|
| Symbol** | Å | $10^6 r^{-6}$ | $n$ | $10^6 n r^{-6}$ |
| $r_1$ (GG′) | 4.828 | 78.958 | 2 | 157.916 |
| $r_2$ (GA) | 5.577 | 33.235 | 2 | 66.470 |
| $r_3$ (GA′) | 7.376 | 6.210 | 4 | 24.840 |
| $r_4$ (GB) | 9.411 | 1.439 | 2 | 2.878 |
| $r_5$ (GB′) | 10.58 | 0.713 | 4 | 2.852 |
| $r_6$ (GC) | 10.23 | 0.878 | 2 | 1.756 |
| $r_7$ (GC′) | 11.30 | 0.480 | 4 | 1.920 |
| $r_8$ (GD) | 11.61 | 0.408 | 2 | 0.816 |
| $r_9$ (GD′) | 12.57 | 0.254 | 4 | 1.016 |
| $r_{10}$ (GA″) | 11.15 | 0.520 | 4 | 2.080 |
| $r_{11}$ (GA$_2$′) | 12.15 | 0.311 | 4 | 1.244 |
| $r_{12}$ (GE) | 13.80 | 0.145 | 2 | 0.290 |
| $r_{13}$ (GE′) | 14.62 | 0.102 | 4 | 0.408 |
| $r_{14}$ (GF) | 15.12 | 0.084 | 2 | 0.168 |
| $r_{15}$ (GF′) | 15.85 | 0.063 | 4 | 0.252 |
| | | Total | 46 | 264.906 |

* $r_1 = b_0/2$
$r_2 = \frac{1}{2}(r_6^2 + r_8^2 - 0.9696\ r_6 r_8)^{1/2}$
$r_3 = (r_1^2 + r_2^2)^{1/2}$
$r_4 = \frac{1}{2}(r_6^2 + r_8^2 + 0.9696\ r_6 r_8)^{1/2}$
$r_5 = (r_1^2 + r_4^2)^{1/2}$
$r_6 = c_0$
$r_7 = (r_1^2 + r_6^2)^{1/2}$
$r_8 = a_0$
$r_9 = (r_1^2 + r_8^2)^{1/2}$
$r_{10} = (4r_1^2 + r_2^2)^{1/2}$
$r_{11} = (r_1^2 + 4r_2^2)^{1/2}$
$r_{12} = (r_2^2 + r_6^2 + 0.9696\ r_2 r_6)^{1/2}$
$r_{13} = (r_2^2 + r_{12}^2)^{1/2}$
$r_{14} = (r_2^2 + r_8^2 + 0.9696\ r_2 r_8)^{1/2}$
$r_{15} = (r_1^2 + r_{14}^2)^{1/2}$

** Every single primed letter indicates the same position of $Gd^{3+}$ on the upper or lower adjoining plane, and the double primed letter indicates the plane next to the adjoining plane. GA$_2$′ represents a distance twice as long as GA′.

Firstly, every tripositive ion should settle in an electrostatic balancing position. Secondly, the closest arrangement of the heaviest gadolinium ion should reflect the most intensive X-ray diffraction. Lastly, the hydrogen bonding between oxalate ions and water molecules would as usual have a habit of forming the framework of a monoclinic cell.[9,10] The locations of 46 nearest neighboring ion pairs of gadolinium are shown in Figure 1, and the $r$-values of each of the ion pairs are summarized in Table 2. In providing these locations and $r$-values, due consideration has been given and a geometrical allowance has also been made.

The sum of the summation terms in Eq. (4) gives the value $264.9 \times 10^{-6}$, from which the theoretical value $\langle \Delta H^2 \rangle$ is calculated to be $8.630 \times 10^5$ gauss$^2$.

$$\langle \Delta H^2 \rangle_{\text{calc}} = 3.258 \times 10^9 \times 264.9 \times 10^{-6}$$
$$= 8.630 \times 10^5 \text{ gauss}^2$$

The experimental value of the equivalent magnetic field second moment is computed by referring to the corresponding ESR differential curve. The width between the points of maximum slope is measured and calculated to be 1850 gauss (average). The value for $\langle \Delta H^2 \rangle$ thus obtained is $8.626 \times 10^5$ gauss$^2$. Since a good agreement exists between the observed second moment and that calculated theoretically, the validity of the suggested model representing the location of gadolinium ions in the hydrated gadolinium oxalate is well justified.

**C. Location Diagram.** Referring to Fig. 1, we see that each pair of the gadolinium ions lies on the diagonal of a parallelogram in the *a*—*c* plane. Each ion rides on the head of the other, and a total of four gadolinium ions in a unit cell with the coordinates (¼ 0 ¼), (¾ 0 ¾), (¼ ½ ¼), and (¾ ½ ¾) constitute the $\bar{1}01$ plane. One of the densest packed planes with gadolinium ions is 020 plane, which gives rise to the strongest diffractions throughout the experiment. Another characteristic of the packing is that each gadolinium ion is located at the center of gravity of a parallelogram. Both the upper and lower planes are similarly packed, hence the ions coexist centrosymmetrically around G.

The method for locating ions in salts in this experiment has one great advantage, *viz.*, exchange interactions contribute nothing to the second moment. Moreover, this method reveals immediately whether the assumption is correct. Decision is very easy owing to the extreme sensitiveness of the summation term of $r^{-6}$. If 1 per cent error was made in estimating the smallest $r$-value, such as $r_1$ in Table 2, the error of the result would be over 5 per cent. If an incorrect position was so assigned that in the unit cell of gadolinium oxalate decahydrate two $Gd^{3+}$ ions were located on the longer diagonal at (¼ 0 ¾) and (¾ 0 ¼), and the other two on the shorter at (¼ ½ ¼) and (¾ ½ ¾), the calculated second moment compared with the experimental result would have been too low, with a discrepancy of more than 30 per cent. Another remarkable feature of this method is that the smallest $r$-value has a decisive influence on the second moment. It is readily seen from Table 2: the shortest distance $r_1$ (2 ions) has an effect as much as 60 per cent; the next two distances $r_2$ and $r_3$ (6 ions) 34 per cent; whereas all the others, from $r_4$ to $r_{15}$ (38 ions), only 6 per cent of the grand total. Such a characteristic may serve as a convenient guide leading to the right assignment of location of ions in a crystal.

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[9] F. R. Ahmed and D. W. J. Cruickshank, *Acta Crystallgr.*, **6**, 385 (1953).

[10] G. A. Jeffrey and G. S. Parry, *J. Amer. Chem. Soc.*, **76**, 5283 (1954).

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