Magnetic Study of the Heavier Rare-Earth Iron Garnets

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Magnetic measurements, over the temperature range 1.4–298°K, have been made on ultrapure crystals of the heavier rare-earth (Gd to Yb) iron garnets, allowed to rotate freely in the magnetic field. Measurements in the same temperature range have also been made on polycrystalline Lu iron garnet. At temperatures near 1.4°K, the iron garnets of Gd, Tb, Dy, and Ho are apparently magnetically saturated at moderate fields, while those of Er, Tm, and Yb are not saturated at such fields, nor at 4.2°K to a field of $\approx$80 kOe. The polycrystalline Lu iron garnet appears to be magnetically saturated over the whole temperature range investigated at a field $\leq$9.9 kOe. In all cases in which saturation was not attained, the behavior of the moment versus field was linear, and spontaneous magnetizations were obtained by extrapolation of moment versus field to zero field. Except for the Er and Yb iron garnets, all 0°K spontaneous magnetizations found in this study are higher than those reported by Pauthenet. For Er iron garnet, a lower value is obtained, possibly because of extrapolation of moment versus field to zero instead of infinite field. Tm iron garnet does not have a compensation point and Yb iron garnet appears to be compensated from 0 to $\sim$6°K.

INTRODUCTION

THE magnetic behavior of the heavier rare-earth (Gd-Lu) iron garnets (IG) was first reported by Pauthenet.[1] However, this work was done on polycrystalline materials. At least in some cases, these materials were not of the purity presently possible. Further, the large anisotropy introduced by some of the rare-earth ions made it difficult to determine the true spontaneous magnetizations at low temperatures. Single crystals of most of the heavier rare-earth garnets have now been prepared from ultrapure materials[2] on which our measurements have been made.

Results of our study of the behavior of the lighter rare-earth (La-Eu) ions in the iron garnets have been reported earlier.[3]

EXPERIMENTAL

Magnetic measurements were made over the temperature range 1.4–298°K with a pendulum magnetometer[4] to fields of 15.3 kOe. Usually measurements were made on one or more single crystal spheres allowed to rotate freely in the magnetic field. However, difficulty in obtaining sizable crystals of YbIG and LuIG forced us to use YbIG crystals of arbitrary shape and polycrystalline LuIG, in which case anisotropy is not large.

High-field measurements to 80 kOe were made at 4.2°K using the Bitter-type magnet and an extraction method for the determination of the moment. Such measurements were made only on the garnets which did not appear to be magnetically saturated at the moderate fields.

MAGNETIC DATA

Gadolinium Iron Garnet

The gadolinium iron garnet crystals were magnetically saturated at $\approx$12 kOe between 1.4 and 12°K. At temperatures $\geq$22°K, magnetic saturation was not attained, but for each temperature the behavior of magnetization versus temperature was linear and spontaneous magnetizations were obtained by extrapolating n_B versus H_a to $H_a=0$. At 1.4°K, the saturation magnetizations of a number of specimens from the same batch of crystals was $15.93\pm0.03\,\mu_B$. The expected 0°K spontaneous magnetization is, of course, $16.00\,\mu_B$

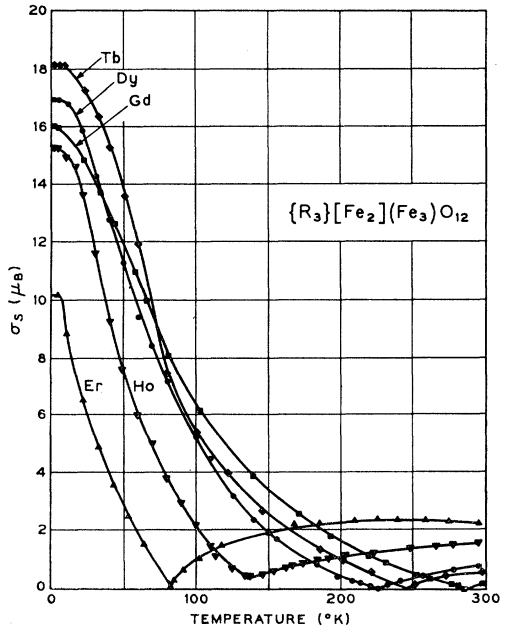

FIG. 1. Spontaneous magnetization in Bohr magnetons per formula unit versus temperature of Gd, Tb, Dy, Ho, and Er iron garnets.

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[1] R. Pauthenet, Ann. Phys. (Paris) **3**, 424 (1958).
[2] J. P. Remeika, (to be published).
[3] S. Geller, H. J. Williams, R. C. Sherwood, J. P. Remeika, and G. P. Espinosa, Phys. Rev. **131**, 1080 (1963).
[4] R. M. Bozorth, H. J. Williams, and D. E. Walsh, Phys. Rev. **103**, 572 (1956).

per formula unit, the value we had obtained earlier[5] by extrapolation of n_B versus $1/H_a$ to $1/H_a=0$ on polycrystalline material. A new polycrystalline specimen of high purity was tested again at 1.4°K and again the value obtained by this extrapolation was 16.00 μ_B. The slope of n_B versus $1/H_a$ was small, the value of n_B obtained at 15.3 kOe being 15.94 μ_B. We are forced to conclude from this that a very small amount of the flux is included in these crystals, amounting to about 0.6% by weight. The spontaneous magnetization versus temperature plot shown in Fig. 1 has been corrected by the factor 16.00/15.93. Actually this is hardly noticeable on the scale of this plot.

Terbium, Dysprosium, and Holmium Iron Garnets

The crystals of these garnets were apparently magnetically saturated at ~9, ~13.4, and ~13.4 kOe at temperatures 1.4 to 8.1, 1.4 and 1.4°K, respectively. Above these temperatures, saturation was not attained at fields $\leq$15.3 kOe, and again it was possible to obtain spontaneous magnetizations at each measurement temperature by extrapolation of n_B versus H_a to $H_a=0$. Plots of spontaneous magnetization versus temperature for these garnets are given in Fig. 1.

Erbium Iron Garnet

The crystals of this garnet were not saturated at any temperature at fields below 15.3 kOe. Measurements at 4.2°K to a field of 78 kOe showed that n_B versus H_a at this temperature behaved essentially linearly in this range. Extrapolation to $H_a=0$ gave a spontaneous magnetization at 4.2°K of 10.2 μ_B per formula unit. At 78 kOe the magnetization was 12.1 μ_B.

Thulium Iron Garnet

Crystals of this garnet were not magnetically saturated at any temperature at fields below 15.3 kOe. Spontaneous magnetizations were obtained as for the other garnets when saturation was not attained and are plotted versus temperature in Fig. 2. Measurements at 4.2°K to a field of 80 kOe showed that n_B versus H_a was linear over the whole range 10 to 80 kOe. This line intersected $H_a=0$ at 1.2 μ_B. At 80 kOe the magnetization was 5.1 μ_B.

Ytterbium Iron Garnet

Crystals of this garnet were not saturated over the entire temperature range of measurement. However, at 1.4 and 4.2°K the slopes of n_B versus H_a were identical and considerably larger than at any other temperature between 11.5 and 293°K. For comparison: at 1.4 and 4.2°K, the slope was 0.038 μ_B/kOe; at 11.5°K, 0.0065 μ_B/kOe; at 41.5°K, 0.016 μ_B/kOe; at 80°K, 0.012 μ_B/kOe; at 293°K, 0.0065 μ_B/kOe. At 1.4 and 4.2°K, extrapolation of n_B versus H_a to $H_a=0$ gave 0.00 μ_B. Measurements to 78 kOe at 4.2°K also gave precisely linear n_B versus H_a behavior intersecting $H_a=0$ at 0.00. At 78 kOe, the magnetization was 2.8 μ_B; for these measurements, the slope of n_B versus H_a was 0.036 μ_B/kOe, slightly different from that obtained from the measurements with the magnetometer.

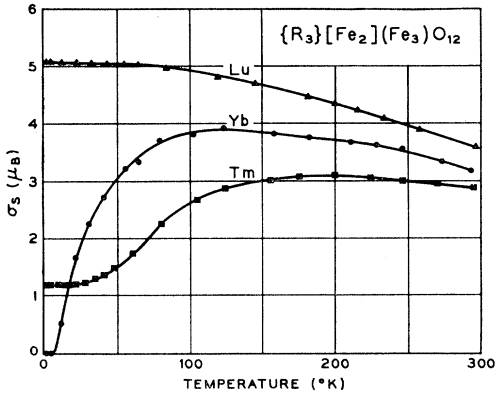

FIG. 2. Spontaneous magnetization in Bohr magnetons per formula unit versus temperature of Tm, Yb, and Lu iron garnets.

Lutetium Iron Garnet

Sizable crystals of this garnet could not be obtained from the ultrapure materials.[2] We therefore made measurements on polycrystalline material made from the ultrapure constituents. Magnetic saturation was attained over the whole temperature range at a field of 9.9 kOe, the lowest field at which measurements were made. (Other measurements were made at fields of 11.9, 13.4, and 15.3 kOe.)

Spontaneous magnetization versus temperature is plotted in Fig. 2. To about 86°K, the spontaneous magnetization is greater than 5.00 μ_B; at 1.4°K it is 5.07 μ_B. Similar behavior was found for a specimen of LuIG made approximately two years ago. The difference, 0.07 μ_B, between observed and theoretical[6] moments at 1.4°K, is significantly outside the experimental error of the magnetic measurements; we have no difficulty in obtaining repeatedly the theoretical value for YIG within 0.2%. It is unlikely (but perhaps not impossible) that the higher moment is characteristic of LuIG or that it is caused by impurities in the starting materials. It is possible that it is caused by a trace amount of impurity phase not observable on the x-ray diffraction powder photograph.

DISCUSSION

In Table I, similar to one given by Pauthenet, we list the 0°K spontaneous magnetizations and compensation points (if any) for the heavy rare-earth iron

[5] S. Geller, H. J. Williams, and R. C. Sherwood, Phys. Rev. 123, 1692 (1961).

[6] L. Néel, Ann. Phys. (Paris) 3, 137 (1958).

TABLE I. Magnetic data for heavier rare-earth iron garnets, $\{R_3\}[Fe_2](Fe_3)O_{12}$.

R	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Number of $4f$ electrons	7	8	9	10	11	12	13	14
L	0	3	5	6	6	5	3	0
$2S$	7	6	5	4	3	2	1	0
$\lvert\sigma_0\rvert, \mu_B \lvert 3(L+2S)-5\rvert$	16	22	25	25	22	16	7	5
$\lvert\sigma_0\rvert, \mu_B$ obs. this work	16.0	18.2	16.9	15.2	10.2	1.2	0	5.07
$\lvert\sigma_0\rvert, \mu_B$ obs. Pauthenet	15.15	15.7	16.25	13.75	11.55	1.0	0	4.16
θ_c, °K, this work	286	246	226	137	83	None	a	
θ_c, °K, Pauthenet	290	246	220	136	84	$4<\theta_c<20.4$		

[a] See text.

garnets. The results obtained by Pauthenet are shown for comparison. The compensation point, 286°K, found in this work for GdIG is in excellent agreement with that, 286°K, found by Geschwind and Walker[7] by a resonance technique. Thus, the disagreement between this value and that found by Pauthenet and his lower 0°K moment indicate the presence of impurity in Pauthenet's garnet phase. However, another cause of the lower moment could be the presence of extraneous phases $GdFeO_3$ and $\alpha-Fe_2O_3$. The same comments may be made regarding Pauthenet's different values of 0°K moment and θ_c for DyIG, although an additional cause could be the inadequacy of the extrapolation of low-field data on the polycrystalline specimen to "infinite field." The agreement of compensation points for the Tb and Ho iron garnets would appear to indicate that Pauthenet's lower moments for these also arise from the inadequacy of this type of extrapolation and/or presence of extraneous phases, but not of impurity in the garnet phase itself. In the ErIG case, again agreement of θ_c's is excellent, but because of the nature of the n_B versus H_a data at low temperatures, we believe that the extrapolation should be made to $H_a=0$ as in the TmIG case.

Our data indicate that TmIG does not have a compensation point, corroborating the conclusion reached by Cohen[8] on the basis of a Mössbauer effect investigation. In fact, Cohen reported average Tm moments of 1.22 ± 0.1 and $0.89\pm0.08\,\mu_B$ in TmIG at 20 and 78°K, respectively. The values we obtain by subtracting the measured TmIG moments at these temperatures from those of YIG are 1.27 and $0.89\,\mu_B$. However, this good agreement does not preclude canting of the Tm moments relative to the [111] direction; Cohen's limits of error allow such canting of about 20°.

In the case of YbIG, although Pauthenet reports a spontaneous magnetization of $0\,\mu_B$ at 0°K, he obtained 0.25 and $0.26\,\mu_B$ at 2.4 and 4.2°K, respectively. We find that the spontaneous magnetizations at 1.4 and 4.2°K are $0.0\,\mu_B$ (see Fig. 1), and in fact appear to be 0.0 from 0 to at least 6°K. Henderson and White[9] have reported that YbIG has a compensation *point* at about 7.5°K. They carried out an experiment in which a crystal was shown to adhere to a magnet below 5.9 and above 8.6°K, but between these temperatures was observed to swing free of the magnet. Now the best physical confirmation of the existence of a compensation *point* is the observation of a 180° turn in the magnetic field when the crystal goes through the compensation point.

We submit that the type of compensation we propose, namely from about 6°K all the way to 0°K, can also lead to the results observed by Henderson and White. The slope of n_B versus H_a is relatively small at 11.5°K where the YbIG is ferrimagnetic. As the temperature decreases to about 6°K (or perhaps slightly higher), the spontaneous magnetization decreases to 0 whereupon the [111] direction abruptly turns 90° to the field because the susceptibility is higher in this new direction. This is the point at which the crystal will momentarily swing away from the magnet. Below 6°K, the high susceptibility of the crystal will cause it to readhere to the magnet.

In the case of LuIG, as already pointed out by Perel and Schieber,[10] there is little doubt that the specimen measured by Pauthenet was impure.

It must be pointed out that of the lattice constants reported for these garnets by Pauthenet, only two, those of Dy and Tm, agree well with those reported by Espinosa.[11] As it is doubtful that the differences were caused by erroneous measurement, this must indicate that at least the other garnets contained substantial amounts of impurities. This appears to be a contradiction to the excellent agreement of some of the compensation points. It is difficult to see how such agreement can be accidental, but it appears that there can be little doubt as to the conclusion that must be drawn from the disagreement of the lattice constants.

It would be expected that the single crystal sphere

[7] S. Geschwind and L. R. Walker, J. Appl. Phys. **30**, 163S (1959).

[8] R. L. Cohen, Phys. Letters **5**, 177 (1963).

[9] J. W. Henderson and R. L. White, Phys. Rev. **123**, 1627 (1961).

[10] J. Perel and M. Schieber, J. Appl. Phys. (Japan) **1**, 243 (1962).

[11] G. P. Espinosa, J. Chem. Phys. **37**, 2344 (1962).

of GdIG would be magnetically saturated at or near 0°K, because the Gd^{3+} ion has $L=0$. The Tb, Dy, and Ho iron garnets are also magnetically saturated at moderate fields at temperatures near 0°K, and these appear to belong to a category in which the rare-earth moments are "locked in" at low-temperatures. On the other hand, increasing the field appears to rotate the Er, Tm, and Yb moments. The boundary of the two categories is $2.5<(L+2S)/2S<3$.

Below the compensation point a spherical crystal of ErIG allowed to rotate freely in a magnetic field will be aligned along a [111] direction with the largest components of the Er ion moments in the direction of the field. However, it is probable that the net moments of the Er ions make angles with the [111] direction.[12] Thus, increasing the field tends to rotate these moments into closer parallelism with the easy direction causing a linear increase in the garnet moment with increasing field.

In the case of TmIG, the Tm moments oppose the applied field. Increasing the field appears to rotate the Tm moments such that they *tend* to become perpendicular to the field and finally tend to parallelism with the field at fields of ~80 kOe and above.[13]

In the case of YbIG, at temperatures below about 6°K, the net moment of the Yb sublattices balances the net moment of the iron sublattices. Thus, the easy [111] direction of the YbIG crystal will be perpendicular to the applied field at temperatures below 6°K. The behavior with increasing field will be that of an antiferromagnet, the net moments of the Yb and Fe sublattices will tend to rotate into the direction of the field with increasing field. Somewhat above 6°K, the spontaneous magnetization of YbIG rises rapidly (see Fig. 2) and the crystal rotates so that the [111] direction becomes parallel to the applied field. Above 6°K, the slopes of the magnetization versus H_a at given temperatures are smaller than below 6°K giving further credibility to the interpretation.

Wolf *et al.*,[12] in an elegant calculation of the effect of crystal field on the Yb^{3+} ion moments, arrived at a predicted value of 0.01 μ_B for the 0°K spontaneous magnetization of YbIG in excellent agreement with the value obtained experimentally.

Herpin, Koehler, and Mériel[14] have made a neutron diffraction investigation on a polycrystalline specimen of HoIG. Their results are in agreement with the conclusion advanced by Wolf *et al.*[12] that the crystal fields in the rare-earth garnets cause canting of the moments of the non-S-state ions relative to the easy direction, usually a [111]. However, their results indicate also that at 4.2°K the net contribution per formula unit of the Ho^{3+} ions in the [111] direction is 16.2 μ_B, which implies a spontaneous magnetization for HoIG of 11.2 μ_B. This value is substantially lower than that observed. It is probable that a similar investigation of single crystals would yield better values of the moments.

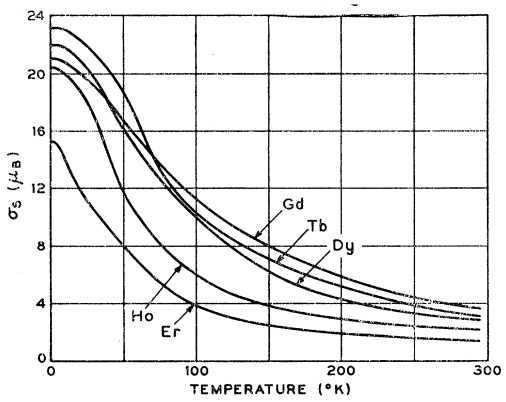

FIG. 3. Average contribution per formula unit to the spontaneous magnetization by the rare-earth ion sublattice versus temperature in Gd, Tb, Dy, Ho, and Er iron garnets.

In Figs. 3 and 4, we show the average contribution of the rare-earth sublattice (per formula unit) obtained by assuming that the contribution of the iron sublattices in each case is the same as that in YIG. In Fig. 5, we plot the theoretical[15] Jg values for the rare-earth ions and show the 0°K measured contributions of each rare-earth ion to the easy-direction spontaneous magnetizations of the garnets. For Gd the expected value is obtained. The lighter rare earths

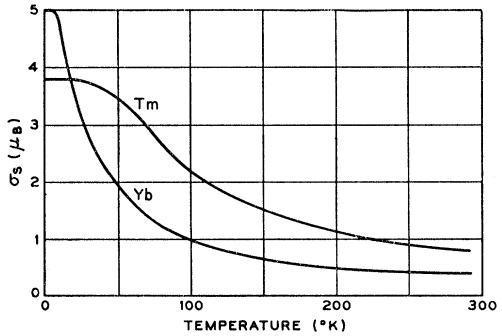

FIG. 4. Average contribution per formula unit to the spontaneous magnetization by the rare-earth ion sublattice in Tm and Yb iron garnets.

[12] W. P. Wolf, M. Ball, M. T. Hutchings, M. J. M. Leask, and A. F. G. Wyatt, J. Phys. Soc. Japan **17**, Suppl. B-I, 443 (1962).

[13] It has been suggested that an alternative source of the linearly increasing magnetization is the presence of a Van Vleck temperature-independent susceptibility resulting from the coupling of ground and excited states of the Tm^{3+} ion through matrix elements of the magnetic moment operator [see also W. P. Wolf, in Rept. Progr. Phys. **24**, 242 (1961)]. The susceptibility does indeed appear to be temperature independent below about 30°K. A precise explanation may ultimately require contribution from both sources. It is probable that a neutron diffraction investigation of a TmIG crystal subjected to magnetic fields of two or more magnitudes can resolve this problem.

[14] A. Herpin, W. C. Koehler, and P. Mériel, Compt. Rend. **251**, 1359 (1960).

[15] F. Hund, Z. Physik **33**, 855 (1925).

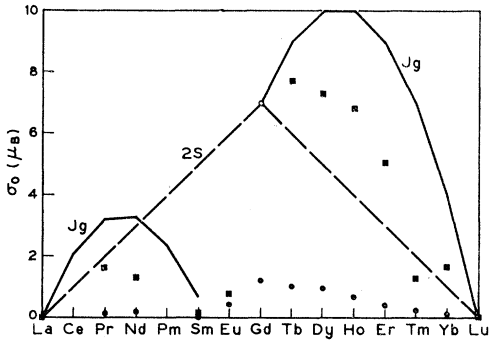

FIG. 5. Observed 0°K (■) and 298°K (●) values of the average moments of the rare-earth ions compared with the theoretical Jg and spin-only values.

have been discussed elsewhere[3]; it will be noted that all contributions of these ions are lower than the spin-only values, although that of Pr is close to the spin-only value of $2\mu_B$. The behavior of the Eu ion has been interpreted by Wolf and Van Vleck.[16] The average contribution of the Tm ion is lower than that of the spin-only value and the contributions of the other heavier ions, Tb, Dy, Ho, Er, and Yb lie between the spin-only and Jg values. At least partly, this is the result of the canting of the moments of these ions relative to the easy direction.

The behavior of the contributions to the spontaneous moments by the heavier rare-earth ions at higher temperatures differs from that at 0°K. At room temperature (see Fig. 5), they decrease monotonically from Gd to Lu.

ACKNOWLEDGMENT

We wish to thank L. R. Walker for helpful discussions.

[16] W. P. Wolf and J. H. Van Vleck, Phys. Rev. **118**, 1490 (1960).

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Nearest-Neighbor Splitting of the Luminescence Levels of ZnS_xSe_{1-x}†

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The gradual shift of ZnS_xSe_{1-x} luminescence levels toward the valence band with decreasing x is attributed to replacement of S by Se in the activator surround. If the center wave function is confined mainly to the four anions surrounding the activator, the center level should split into five levels corresponding to centers with surrounds containing j S atoms and $4-j$ Se atoms. These five j levels are not inconsistent with the gradual level shift toward the valence band. If the five levels are fitted to this shift, emissions from different j levels are not resolved and combine to form a composite broadened band that shifts gradually with x. The broadening of the composite band agrees with that observed for the green bands for Ag, Cu, and self-activation. It also accounts for band crossovers through the terminal ZnSe band and for sliding sidewise emission shifts with quenching reported for Ag activation. The Ag blue band is narrower than calculated for five j levels. Possible explanations are that the blue-center wave function extends to additional anions beyond the nearest neighbors or that the blue emission is partly absorbed at green centers.

INTRODUCTION

IN a mixed crystal such as ZnS_xSe_{1-x}, the anion sublattice is not unique, and impurity levels should be split according to their different anion surrounds. Monovalent cation impurities are incorporated substitutionally at Zn sites and form deep acceptor centers. Insofar as the center wave function is confined mainly to the four anions surrounding the impurity, the center level should be split into five levels corresponding to centers with surrounds containing j S atoms and $4-j$ Se atoms. It is shown that this splitting accounts for certain fetures of ZnS_xSe_{1-x} emission spectra.

The review of ZnS phosphors given by Klasens[1] is excellent for the purposes here, although the covalent nature of the binding could have been emphasized more; see the discussion by Prener and Williams.[2] Emission commonly occurs in broad bands. These bands are more characteristic of the host lattice than of the particular activating impurity. For example, the emission bands of Cu-, Ag-, and self-activated ZnS all have about the same shape and width, all peak in the range from 2.3 to 2.8 eV, and all shift gradually to lower $h\nu$ with decreasing x in $Zn_xCd_{1-x}S$ and ZnS_xSe_{1-x}. These behaviors are possible because the deep acceptor state that is the luminescence center is formed mainly from host-crystal anions surrounding the activator. The activator perturbs the anions to form this state.

Figure 1 shows the positioning in the forbidden gap

† Research sponsored by the U. S. Air Force Cambridge Research Laboratories, Office of Aerospace Research, under Contract No. AF19(628)-3866.

[1] H. A. Klasens, J. Electrochem. Soc. **100**, 72 (1953).

[2] J. S. Prener and F. E. Williams, J. Electrochem. Soc. **103**, 342 (1956).