[CONTRIBUTION FROM THE WESTINGHOUSE RESEARCH LABORATORIES]

A Study of the System $\mathrm{Li_xMn_{(1-x)}Se}$

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The system $\mathrm{Li_xMn_{(1-x)}Se}$ has been prepared by reacting $\mathrm{Li_2Se}$, Se and MnSe in the proper amounts at elevated temperatures. As a preliminary step in this work, a method of preparing pure $\mathrm{Li_2Se}$ was developed. In the range of composition of the Li $\mathrm{Mn_{(1-x)}Se}$ system where $0 \leqslant x \leqslant 0.11$ the product is a single phase material of rock salt structure, its lattice parameter decreasing linearly with composition. Beyond this limit the additional phases $\mathrm{Li_2Se}$ and Se are present. The position of the phase boundary has been confirmed by magnetic measurements. The introduction of Li into the MnSe crystal lattice induces ferromagnetism at liquid nitrogen temperature, the saturation magnetization increasing rapidly with the lithium content.

Introduction

In several earlier papers[1-3] the authors have reported on the preparation and the electrical and magnetic properties of some lithium substituted transition metal monoxides. One of the primary reasons for studying these materials concerned their magnetic properties. It was expected on the basis of the Zener[4] double exchange mechanism that these materials should be both ferromagnetic and good electrical conductors. However, no ferromagnetism was found in any of the systems studied, *i.e.*, $\mathrm{Li_xMn_{(1-x)}O}$ $(0 \leqslant x \leqslant 0.35)$, $\mathrm{Li_xCo_{(1-x)}O}$ $(0 \leqslant x \leqslant 0.2)$, $\mathrm{Li_xNi_{(1-x)}O}$ $(0 \leqslant x \leqslant 0.15)$, or $\mathrm{Li_xCu_{(1-x)}O}$ $(0 \leqslant x \leqslant 0.02)$.

In the study of the electrical conductivity of the lithium substituted transition metal monoxides, the conductivity always was found to require an energy of activation. This activation energy was interpreted as the energy required to relieve distortions around the site of a triple plus cation and permit electron transfer to occur. Since in double exchange the electron transfer proceeds without activation, it appears that this interaction does not occur in these substituted oxides.

It has been predicted[3,5] that the activation energy should decrease as the electronic polarizabilities of the ions increase. Selenium is more easily polarized than oxygen. Thus it follows that $\mathrm{Li_xMn_{(1-x)}Se}$ should have a lower activation energy for electrical conductivity than $\mathrm{Li_xMn_{(1-x)}O}$. If the activation energy were to disappear completely, double exchange should result, giving rise to ferromagnetism.

From an empirical standpoint, the same prediction might be made. The resistivity of MnSe is much smaller than that of MnO. Also, the activation energy for electrical conductivity is smaller in manganese selenide.[6,7] In the earlier work on the lithium substituted transition metal oxides,[2] it was found that lithium substitution decreased both the activation energy and resistivity from that of the parent oxide. Thus it should be expected that $\mathrm{Li_xMn_{(1-x)}Se}$ would exhibit very low values for these two terms. If the activation energy were to vanish, it is possible that the double exchange interaction would occur.

With this information in mind, a study of the $\mathrm{Li_xMn_{(1-x)}Se}$ system was undertaken. Although lithium substituted MnSe has not been made previously, MnSe is known and can be prepared with a rock salt crystal structure.[8] Thus a direct comparison is possible with MnO which is also a rock salt structure.

Discussion

The $\mathrm{Li_xMn_{(1-x)}Se}$ system was prepared according to the equation

$$\frac{x}{2}\,\mathrm{Li_2Se} + \frac{x}{2}\,\mathrm{Se} + (1-x)\mathrm{MnSe} \longrightarrow \mathrm{Li_xMn_{(1-x)}Se}$$

The powdered reactants were fired in graphite or MgO crucibles which were contained in sealed Vycor tubes. Lithium selenide was used in this reaction rather than lithium and selenium metals in order to avoid the violent exotherm accompanying their reaction.

X-Ray diffraction patterns were taken of the products. The results are shown in Fig. 1. The products are single phase rock salt structures in the region $0 \leqslant x \leqslant 0.10$. The lattice parameter can be seen to decrease linearly with lithium content. The magnitude of the decrease in lattice parameter between $x = 0$ and $x = 0.1$ is almost exactly that found in the $\mathrm{Li_xMn_{(1-x)}O}$ system (0.021 *vs.* 0.0205 Å.). This implies that the same ionic radii for the cations apply in both cases and that the anions are not touching.

In order to prove that this decrease in lattice parameter represents the formation of the phase $\mathrm{Li_xMn_{(1-x)}Se}$ as described above and not cation or anion defect structures of MnSe, preparations were made of $\mathrm{MnSe_{1.01}}$ and $\mathrm{MnSe_{0.99}}$ at 650° using vacuum distilled manganese. All materials were handled in a dry box. The X-ray patterns showed predominantly MnSe with traces of $\mathrm{MnSe_2}$ and Mn, respectively. The lattice parameters of the MnSe phases are within experimental error of the parameter for pure MnSe, thus eliminating the possibility that cation and anion defects might result in the decrease in lattice parameter and indicating that the range of stoichiometry of the MnSe phase is very small.

In order to prove that $x/2$ Se was required in addition to $x/2$ $\mathrm{Li_2Se}$ and $(1-x)$MnSe, a sample of nominal composition $\mathrm{Li_{0.1}Mn_{0.9}Se_{0.95}}$ was prepared from 0.05 $\mathrm{Li_2Se}$ and 0.9 MnSe. The product ac-

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(1) W. D. Johnston and R. R. Heikes, THIS JOURNAL, **78**, 3255 (1956).

(2) R. R. Heikes and W. D. Johnston, *J. Chem. Phys.*, **26**, 582 (1957).

(3) W. D. Johnston and R. R. Heikes, *J. Chem. Phys. Solids*, to be published.

(4) C. Zener, *Phys. Rev.*, **82**, 403 (1951).

(5) C. Zener and R. R. Heikes, Conference on Magnetism and Magnetic Materials, 216 (1956). American Institute of Electrical Engineers, 33 West 39th Street, New York 18, New York.

(6) W. Palmer, *J. App. Phys.*, **25**, 125 (1954).

(7) M. Marakami, *Bull. Fac. Engr. Hiroshima Univ.*, **2**, 67 (1953).

(8) A. Baroni, *Z. krist.*, **99A**, 336 (1938).

cording to visual examination was two phase, the major phase black and presumably MnSe, and the other phase orange-red and presumably Li_2Se, indicating that little or no reaction occurred. In this case there is a small decrease in the lattice parameter of the unit cell from that of pure MnSe, indicating that a minor change has taken place in the MnSe crystal lattice. However, as can be seen from Fig. 1, the parameter is far from that of $Li_{0.1}Mn_{0.9}Se$. Actually the parameter reflects a value of $x = 0.025$. The presence of a small excess of Se in the MnSe can account for this value. One way in which such an excess could arise is from small quantities of oxygen in the manganese metal used to prepare MnSe. Using manganese which was distilled *in vacuo* and ground in argon to minimize oxidation, a new sample of MnSe was prepared. A sample of $Li_{0.1}Mn_{0.9}Se_{0.95}$ prepared from this material gives a parameter which is somewhat higher, reflecting a value of $x = 0.012$. This change suggests that oxygen impurities are the cause of this anomaly, but that all sources of oxygen impurity have not been eliminated, *e.g.*, oxygen in Li_2Se, Se and the reaction container. Such sources of oxygen would react with MnSe or Li_2Se *in situ* and release a small excess of selenium.

Beyond $x = 0.15$ in the $Li_xMn_{(1-x)}Se$ phase the lattice parameter remained essentially constant. This behavior is indicative of a phase boundary in the range $0.10 < x < 0.15$. By extending both of the straight line portions of the graph of lattice parameter *vs.* composition until they intersect, the position of the phase boundary can be established as occurring at $x = 0.11$.

It was disturbing to note that preparations where $x = 0.15$, 0.20 and 0.30 did not show a second phase in the X-ray patterns. Only where $x = 0.5$ did a second phase appear. It was Li_2Se. It was noted, however, that in all cases the MgO crucibles used in these experiments were stained red-black. the amount of staining increasing with x. The stain was found to be predominantly Li_2Se with traces of Se and $MnSe_2$. No $Li_xMn_{(1-x)}Se$ was found in this residue. To investigate this further a number of preparations were made using graphite crucibles. In these cases Li_2Se was found in the products where $x > 0.11$. From this it appears that MgO acts to purify the $Li_xMn_{(1-x)}Se$ phase by physically absorbing the impurity phases which probably exist as a liquidus at the reaction temperature. The graphite on the other hand is not wet by the impurity phases and the products are not separated.

Analytical data in Table I support the physical separation by MgO of the saturated $Li_xMn_{(1-x)}Se$ from the additional phases in the multiple phase region. It will be noted that the analytical data cited for $Li_{0.2}Mn_{0.8}Se$ and $Li_{0.3}Mn_{0.7}Se$ prepared in MgO are not close to the nominal composition, but reflect a composition very nearly equal to the phase boundary material $Li_{0.11}Mn_{0.89}Se$.

It remains to inquire into the nature of the multiple phase region. It appears that three phases must be involved. The saturated phase $Li_{0.11}Mn_{0.89}Se$ is of course present. In addition, Li_2Se is always present. The remaining phase may be Se or $MnSe_2$. Selenium normally cools from the melt as a glass[9] and gives no diffraction pattern. It has been observed *via* X-rays in only one of these samples. However, on the basis of the red-black deposit on the MgO crucible, it is a likely possibility. In addition, small amounts of $MnSe_2$ have been observed in several cases. The following equations may be used to represent these two possibilities

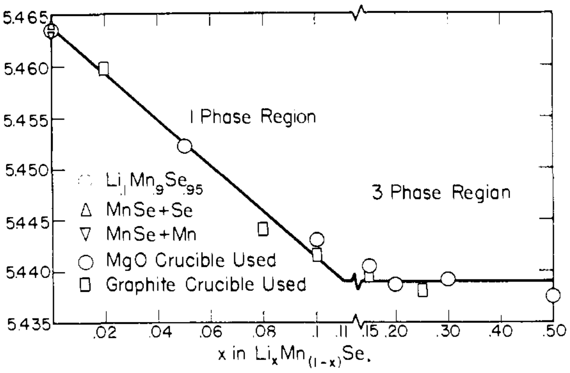

Fig. 1.—X-Ray lattice parameter *vs.* composition.

$$\frac{x}{2}\,Li_2Se + \frac{x}{2}\,Se + (1 - x)MnSe \longrightarrow Li_xMn_{(1-x)}Se \quad \text{(nominal)}$$

$$\text{(I)}\quad \frac{1-x}{1-z}\,Li_zMn_{(1-z)}Se + \frac{x-z}{2-2z}\,(Li_2Se + Se) \longleftarrow$$

$$\text{(II)}\quad \frac{2-3x}{2-3z}\,Li_zMn_{(1-z)}Se + \frac{x-z}{2-3z}\,(Li_2Se + MnSe_2) \longleftarrow$$

x = nominal composition parameter
z = phase boundary composition parameter = 0.11

The selective absorption of the impurity phases by the MgO crucible may be used to determine which phases are present beyond the phase boundary. Using a pellet of nominal composition $Li_{0.5}Mn_{0.5}Se$ weighing 2.7180 g., it may be calculated that in case I the weight transfer from the pellet to the MgO should be 0.94 g. In case II the transfer should be 1.78 g. Actually the pellet was observed to lose 0.99 g. and the MgO took up 0.95 g., which values are in close agreement with the predicted value for case I. Admittedly such a separation should not be expected to be quantitative, and indeed in this case it was not complete as indicated by the presence of Li_2Se in the pellet as detected by X-ray. Accordingly additional confirmation was required.

Further evidence concerning the choice between products I and II in the multiple phase region may be made by referring to the magnetic data obtained on this system. It may be observed from Fig. 2 that MnSe in which lithium has been substituted exhibits ferromagnetism at liquid nitrogen temperatures. A discussion of the theory of the ferromagnetism will be deferred to a succeeding paper, but it must be pointed out that the value of $\sigma_{77°K.}$ the saturation magnetization at 77°K., increases with lithium till the maximum lithium concentration in the single phase region is reached. It then decreases due to the dilution of the ferromagnetic phase boundary composition, $Li_{0.11}Mn_{0.89}Se$, by the impurity phases. In the multiple phase region the

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(9) B. D. Cullitz, M. Telkes and J. T. Norton, *AIMEE Metals Trans.*, **188**, 47 (1950).

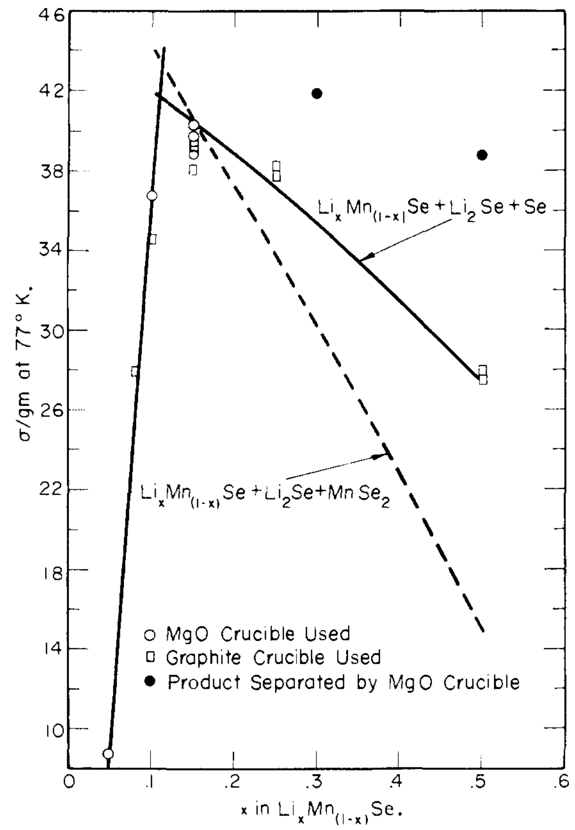

Fig. 2.—Saturation magnetization at 77°K. *vs.* composition.

saturation magnetization may be represented by equations corresponding to cases I and II.

$$\text{(I)}\quad \sigma/\text{g.} = \sigma/\text{g. } \mathrm{Li}_z\mathrm{Mn}_{(1-z)}\mathrm{Se}\ \frac{\frac{1-x}{1-z}MW_{\mathrm{Li}_z\mathrm{Mn}_{(1-z)}\mathrm{Se}}}{MW_{\mathrm{Li}_x\mathrm{Mn}_{(1-x)}\mathrm{Se}}}$$

$$\text{(II)}\quad \sigma/\text{g.} = \sigma/\text{g. } \mathrm{Li}_z\mathrm{Mn}_{(1-z)}\mathrm{Se}\ \frac{\frac{2-3x}{2-3z}MW_{\mathrm{Li}_z\mathrm{Mn}_{(1-z)}\mathrm{Se}}}{MW_{\mathrm{Li}_x\mathrm{Mn}_{(1-x)}\mathrm{Se}}}$$

In each case the equations can be adjusted to the experimental data to give the dependence of saturation magnetization on composition in the multiple phase region. The theoretical curves have been fitted to the data at $x = 0.15$ and $\sigma = 40.5$. As can be seen from the figure, case I fits the data, while case II does not, and thus the second and third phases are Li_2Se + Se. It should also be noted that the theoretical curve for case I intersects the curve of the experimental data in the single phase region at the phase boundary suggested by the X-ray study, $x = 0.11$.

It also may be deduced from this graph that $\sigma_{77°\text{K.}}$ for $Li_{0.11}Mn_{0.89}Se$ is 41.7 c.g.s./g. It is interesting to note that the nominal compositions $Li_{0.2}Mn_{0.8}Se$ and $Li_{0.3}Mn_{0.7}Se$ have values of $\sigma_{77°\text{K.}}$ of 41.9 and 42 c.g.s./g., respectively, which are far above the derived curve and the other experimental points. These values are very nearly equal to the value of σ deduced for the phase boundary material. It will be remembered that these two samples were those prepared in MgO and which, according to X-ray, chemical analysis and weight loss data have been "purified" of Li_2Se + Se, leaving only the phase boundary composition. The agreement of the saturation magnetization data substantiates the belief that Li_2Se and Se have been separated from $Li_{0.11}Mn_{0.89}Se$ by absorption in MgO. The separation in the case of the sample of $Li_{0.5}Mn_{0.5}Se$ was not complete as noted earlier. Thus the saturation of the product obtained in this case is somewhat lower than that of $Li_{0.2}Mn_{0.8}Se$ and $Li_{0.3}Mn_{0.7}Se$, although it is still considerably higher than that of $Li_{0.5}Mn_{0.5}Se$ prepared in graphite.

The position of the phase boundary has been found to be rather insensitive to temperature. Samples of $Li_{0.25}Mn_{0.75}Se$ prepared in graphite at 550, 650, 750 and 850° show a slight increase in lattice parameter with increased temperature (5.438, 5.438, 5.442 and 5.443 Å., respectively). This corresponds to values of x for the phase boundary of 0.11, 0.11, 0.10 and 0.09, respectively. This decrease in x with increasing temperature is rather uncommon and was not expected.

The small amounts of $MnSe_2$ noted in the X-ray patterns of some of the products is believed to be a low temperature phase formed on cooling the sample from the reaction temperature. The amount of this phase may be increased by annealing a three phase mixture at some low temperature, such as 200°. It is probable that the presence of $MnSe_2$ could be eliminated by more rapid cooling from the preparation temperature.

No new phase of the type $LiMnSe_2$ has been observed. This type of compound has been reported in the case of some of the analogous oxides $LiMnO_2$, $LiCoO_2$ and $LiNiO_2$.[1,3,10]

Although a complete report of the magnetic and electrical studies of these compounds will be published separately, several general statements can be made. The electrical resistivity of these materials is very low ($\sim 10^{-3}$ ohm-cm. at $x = 0.05$), and the activation energy for conductivity appears to be absent. This fulfills the requirement for double exchange and, as has been mentioned earlier, results in a ferromagnetic behavior. Such behavior is believed to be due to ferromagnetism and not ferrimagnetism.

Experimental

MnSe was prepared from the powdered elements. The reactants were weighed in the proper amounts, mixed and pressed into pellets. The pellets were sealed in Vycor tubes and fired at 200° for 2 hr., 300° for 2 hr., 550° for 12 hr. and 650° for 24 hr. Belmont electrolytic manganese which was vacuum melted and American Smelting and Refining Company selenium were used. Typical analytical data for MnSe are given in Table I. In several experiments vacuum distilled manganese was used and the powdered reactants were handled under argon. Although no chemical analyses were performed on these samples, it is believed that they were of higher purity.

Lithium selenide was prepared by a new method. This compound had been prepared previously in liquid ammonia.[11] The product of the liquid ammonia preparation was red in color, of unspecified purity and gave broad X-ray diffraction lines.

In the present preparation lithium metal was placed in either a stainless steel or a magnesium oxide boat. The boat was placed in a Vycor tube which contained a reservoir

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(10) L. D. Dyer, B. S. Borie, Jr., and G. P. Smith, This Journal, **76**, 1499 (1954).

(11) E. Zintl, A. Harder and B. Dauth, *Z. Elektrochem.*, **40**, 588 (1934).

TABLE I

ANALYTICAL DATA

Sample	Crucible	Li, %		Mn, %		Se, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
MnSe (Av. of 5)		...	...	41.0	40.6 ± 0.3	59.0	59.8 ± 0.3
$\mathrm{Li_2Se}$ (Av. of 4)[a]		14.95	14.96 ± 0.12	..	...	85.05	84.04 ± .22
$\mathrm{Li_{0.02}Mn_{0.98}Se}$	Graphite	0.10	0.095 ± .005	40.5	40.2 ± .2	...	...
$\mathrm{Li_{0.05}Mn_{0.95}Se}$	MgO	.26	.22 ± .02	39.7	39.2 ± .4	60.0	61.2
$\mathrm{Li_{0.08}Mn_{0.92}Se}$	Graphite	.43	.38 ± .02	38.9	38.7 ± .4	...	...
$\mathrm{Li_{0.1}Mn_{0.9}Se}$	MgO	.54	.50 ± .05	38.3	37.7 ± .1	61.2	61.3 ± .3
$\mathrm{Li_{0.15}Mn_{0.85}Se}$	MgO	.82	...	36.8	36.9	62.3	62.3
$\mathrm{Li_{0.2}Mn_{0.8}Se}$[b]	MgO	1.12	0.57 ± .02	35.4	38.1 ± .4	63.5	61.6
$\mathrm{Li_{0.3}Mn_{0.7}Se}$[b]	MgO	1.74	0.63 ± .00	32.1	38.1 ± .5	65.9	61.7

[a] Also contains 0.5% $\mathrm{SiO_2 + Fe + Mg}$. [b] Original composition, final composition is $\mathrm{Li_{0.11}Mn_{0.89}Se}$.

of selenium. The tube was sealed and heated at 300°. At this temperature selenium vapor in the tube reacts with the lithium metal forming lithium selenide. About 1–2 days are sufficient for the required amount of selenium to vaporize and react with the lithium. The reaction stops when the composition $\mathrm{Li_2Se}$ is reached even when excess selenium is present in the reservoir. No polyselenides have been noted. The product may grow either as an amorphous mass or in the form of dendrites. It is cream in color. The X-ray pattern is clean and sharp and gives a value for the lattice parameter of 6.002 Å. for the anti-fluorite unit cell compared to the value of 6.017 Å. from the material prepared in liquid ammonia. Analytical data are given in Table I. This material is very air sensitive. It instantly turns a dark red and liberates $\mathrm{H_2Se}$ when exposed to air. Thus it appears that the red color previously reported for this compound was due to decomposed material.

Samples in the $\mathrm{Li_xMn_{(1-x)}Se}$ system were prepared by mixing weighed quantities of $\mathrm{Li_2Se}$, Se and MnSe. The mixture was pressed into pellets and placed in either a magnesium oxide boat or a graphite crucible. This container was then sealed in a Vycor tube and was fired at 550° for 12 hr. and 650° for 24 hr. The sealed container served to contain the volatile selenium as well as to eliminate any possibility of reaction with the air. During the reaction the Vycor was somewhat attacked by the lithium which volatilized along with selenium from the pressed pellets. The material loss from this source has been found to be relatively small. At temperatures above 850° the loss by volatilization becomes more pronounced.

Due to the known air sensitivity of the $\mathrm{Li_2Se}$ and the potential sensitivity of phases in the $\mathrm{Li_xMn_{(1-x)}Se}$ system, all operations were conducted using a Blickman vacuum glove box back filled with welding grade argon. In addition, all samples were stored under argon. Materials in the single phase region of the $\mathrm{Li_xMn_{(1-x)}Se}$ system were found to be stable in air. Coarsely powdered $\mathrm{Li_{0.1}Mn_{0.9}Se}$ exposed to air for two months was not discolored, had no odor and gave no change in its X-ray pattern. However, as might be expected, materials in the three phase region are quite unstable due to the presence of $\mathrm{Li_2Se}$.

Samples ground to a fine powder for X-ray diffraction gave patterns with considerable line broadness. Annealing these powders at elevated temperatures, *e.g.*, 600° in sealed vessels, sharpened the X-ray pictures but also resulted in some loss of lithium. To avoid these two problems samples were ground under liquid nitrogen to avoid the effects of cold working. To accomplish this a mortar and pestle, the sealed sample and a bottle of paraffin oil were placed in a polyethylene bag. This bag was flushed with nitrogen gas. The mortar was then filled with liquid nitrogen and the sample was ground. The sample was then permitted to warm to room temperature under a continuing flow of gaseous nitrogen and was then covered with a small quantity of paraffin oil. The resulting suspension could then be drawn into an X-ray capillary. The sample was mounted in an 11.54 cm. diameter Debye camera. Iron radiation, $K\alpha_1$ and $K\alpha_2$ 1.93597 and 1.93991 Å., was used throughout. The individual values of the lattice parameters plotted on Fig. 1 are believed to be within ±0.0007 Å. In the three phase region where the parameter should be constant, the deviation from an average parameter of 5.439 Å. is found to be ±0.0008 Å.

Chemical analyses were performed by dissolving the sample in acid and precipitating selenium with $\mathrm{SO_2}$. Manganese then was determined by the sodium bismuthate method. Lithium was determined on a separate sample by weighing as the sulfate after the removal of selenium by $\mathrm{SO_2}$ and manganese by the mercury cathode and 8-hydroxyquinoline.

Magnetic measurements were made using the field gradient method with samples sealed in small Pyrex bulbs.

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