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EFFECTS OF LITHIUM AND OXYGEN LOSSES
ON THE MAGNETIC AND CRYSTALLOGRAPHIC
PROPERTIES OF SPINEL LITHIUM FERRITE

by D. H. Ridgley, H. Lessoff, and J. D. Childress

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SUMMARY

The magnetic moment and lattice parameter of stoichiometric spinel lithium ferrite ($\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_{11}$) has been reliably established, respectively, as $3736 \pm 20\text{G}$ at 25°C and $8.3293 \pm 0.0005\text{\AA}$ at 28°C . Under 1 atmosphere of oxygen, lithium ferrite loses both oxygen and lithium oxide in increasing amounts with increasing temperature above about 950 to 1000°C . Slow cooling and annealing at a lower temperature bring about reoxidation and precipitation of $\alpha\text{-Fe}_2\text{O}_3$. Rapid cooling from the sintering temperature leads to anomalously high magnetic moments and lattice parameters; lower temperature anneals and very slow cooling rates produce anomalously low moment values. Intermediate cooling procedures lead to properties intermediate between these properties.

The properties of the resultant product can be explained very satisfactorily on the basis of solid solutions between lithium ferrite and Fe_3O_4 with rapid cooling and on the basis of solid solution between lithium ferrite and $\gamma\text{-Fe}_2\text{O}_3$ with a second phase of $\alpha\text{-Fe}_2\text{O}_3$ on lower temperature annealing and slow-cooling.

It is doubtful whether the second limiting case described above can occur to any appreciable extent because of the tendency of the products to precipitate the excess Fe_2O_3 as $\alpha\text{-Fe}_2\text{O}_3$.

Finally one is led to the following conclusion: The lithium oxide volatilization is associated with oxygen loss under moderate oxygen pressure (~ 1 atmosphere), but the oxygen loss can be shown to be the primary cause of the lithium loss under normal sintering conditions.

I. INTRODUCTION

Although spinel lithium ferrite has been studied by a number of workers (refs. 1-14), the properties of the stoichiometric material remain very much in doubt. Reported magnetic moments

*Presented in part at the Seventieth Annual Meeting, The American Ceramic Society, Chicago, Ill., April 24, 1968 (Electronics Division, No. 34-E-68).

($4\pi M_s$) vary from 2400 (ref. 12) to 3900 gauss (ref. 15), lattice parameters from 8.314 to 8.37 Å (ref. 15), Curie temperatures from 590 to 680°C, and resistivities are reported from a few ohm-centimeters to values many orders of magnitude higher. Prior work on lithium ferrite has been reviewed and summarized by von Alouck (ref. 15). Much consideration has been given to the order-disorder transition occurring near 750°C, but little concern has been shown for the effects of ferrous ion or lack of stoichiometry. Much of the variation in properties can probably be traced to these last factors and, thus, to the preparation techniques. Only occasionally are the materials characterized by x-ray diffraction and rarely are such characterizations reported in detail.

It is generally accepted that lithium volatilizes rapidly from lithium ferrite and similar materials, but the quantitative evidence presented has been limited. This results from the absence of a good analytical method for lithium, the errors of analysis being comparable in many cases to the expected lithium deficiencies.

Strickler and Roy (ref. 10) studied the $\text{Li}_2\text{O}-\text{Fe}_2\text{O}_3$ system and found that the solubility of LiFeO_2 in $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ to be less than 5 percent and probably less than 1 percent. Others (refs. 7,8) have reported studies of materials analyzed and found to have compositions containing large excesses of Li_2O . This discrepancy is not insignificant.

A study of the effects of sintering conditions on the magnetic and crystallographic properties of lithium ferrite was made and are reported in this document. The experimental details are given in section II, the observed results in section III, and the authors' interpretations in section IV.

II. EXPERIMENTAL METHODS

Materials Preparation

All samples were prepared from reagent grade Li_2CO_3 and $\gamma\text{-Fe}_2\text{O}_3$. The $\gamma\text{-Fe}_2\text{O}_3$ was analyzed by standard techniques; the Li_2CO_3 was analyzed by acid titration, which requires the assumption of no significant quantity of metal ions other than lithium. The quantities of Li_2CO_3 and $\gamma\text{-Fe}_2\text{O}_3$ were adjusted in accordance with these analyses.

The calculated amounts of Li_2CO_3 and $\gamma\text{-Fe}_2\text{O}_3$ were combined and milled 8 hours under ethanol in an attritor. This product was dried, passed through a 100 mesh screen, and heated in air at 700°C for 4 hours. The resulting material was remilled under ethanol, as previously, dried, and screened.

This prefired $\text{Li}_2\text{CO}_3\text{-Fe}_2\text{O}_3$ material was fired under 1 atmosphere of oxygen at temperatures from 900 to 1400°C for times varying from 1 minute to 72 hours after the samples reached temperature. The majority of the samples were fired for either 4 or 24 hours. The heat treatments were concluded by varied cooling schedules, including sharp cooling by rapid removal of the samples from the furnace to room ambient conditions, and by controlled cooling under 1 atmosphere of oxygen at rates varying from 20 to 320°C/hr. The sharply cooled and slowly cooled samples for each sintering schedule were heated simultaneously under oxygen, and then one sample container was removed and sharply cooled in air, while the other was cooled slowly at a controlled rate under 1 atmosphere of oxygen. All such samples were characterized by x-ray diffraction and magnetic moment measurements. The previously sharply cooled samples were subsequently annealed in oxygen at 900°C for 8 hours, and then cooled to room temperature at 10°C/hr. The x-ray diffraction and magnetic moment measurements were then repeated.

Magnetic Measurements

Magnetic moments of the products, after the various heating schedules, were determined at room temperature (25°C) using a Princeton Applied Research vibrating sample magnetometer (Foner type) at an applied field of 8 kOe. To reduce the effects of temperature fluctuations, a selected lithium ferrite sample was compared with nickel (99.999%) in a series of a large number of measurements. All products were compared with this one product. The probable error of the individual magnetic measurements is estimated to be about ± 25 G. The value assumed for nickel was 54.39 emu/g.

X-ray Diffraction Measurements

Lattice parameters of all products were determined using a Norelco diffractometer with Cu $K\alpha$ radiation ($K\alpha_1 = 1.54051 \text{ \AA}$, $K\alpha_2 = 1.54433 \text{ \AA}$), and an Advanced Metals Research focusing LiF crystal monochromator in the diffracted beam, a scintillation counter detector, and pulse-height discriminator. Scanning speed was 1/8 deg 2θ /min with a 1-sec time constant; data was recorded as 1 deg 2θ /in. of chart length. Other measurement conditions were: standard flat sample without rotation in the plane of the sample surface; 1 deg divergence slit throughout the scan; horizontal divergence of Soller slits 4.5 deg. Peak angle positions were taken as the highest point of the peak. All x-ray measurements were made at 28°C, the ambient temperature of the room which was found to remain constant to within $\pm 1^\circ\text{C}$. Lattice parameters calculated from the various peaks with $2\theta > 90$ deg were plotted versus $\cos^2 \theta$ and extrapolated to $\cos^2 \theta = 0$. The lattice parameter of one sample was determined by the extrapolation

method and also by use of silicon as internal standard; the values found differed by 0.0005 Å. The lattice parameter of silicon derived from this same scan using the extrapolation method was 5.4308 Å; the I.U.C. value according to Parrish (ref. 16) is 5.43050 at 25°C (5.43054 Å at 28°C after applying the thermal expansion coefficient) without refraction correction. This latter difference (-0.003 Å) was applied as a correction to all extrapolated lattice parameters. This difference is thought to arise primarily from a failure of the lattice parameter values calculated from the individual diffraction peaks to be a true linear function of the extrapolation function $\cos^2 \theta$. The probable error of the lattice parameter measurements is estimated to be ± 0.0005 Å.

III. RESULTS

The effects of the various heat treatments are shown in Figures 1 and 2. In Figure 1 the moment values plotted are not the true $4\pi M_g$ values since the density increases during the heat treatment, as explained in section IV. The values shown are proportional to the moment per unit weight and are the values which would be obtained if the separate products were prepared under those conditions and were assumed to be stoichiometric lithium ferrite. It can be seen that as the sintering temperature is increased, the moments (Figure 1) and the lattice parameters (Figure 2) increase in parallel fashion, both for the sharply cooled and the slowly cooled materials. When the materials originally sharply cooled were annealed at 900°C for 8 hours and then cooled very slowly (10°C/hr), the moments decreased with increase in the temperature of the initial firing, but the lattice parameters decreased to values differing from each other and from the stoichiometric value, 8.3293 Å, only slightly (see section IV).

Each of the x-ray diffraction patterns of the products, after this annealing treatment, showed the presence of α -Fe₂O₃, except the sample sintered at 1000°C for only 4 hours. All those samples heated at 900°C only showed α -Fe₂O₃ in the x-ray patterns, regardless of the time at temperature or the rate of cooling; however, this is regarded as the result of incomplete reaction. Because of the relatively low x-ray scattering amplitude of lithium and oxygen, only rather large amounts of Li₂O (and Li₂CO₃) could be detected by x-ray diffraction methods. No attempt was made to achieve a greater degree of reaction by a series of regrindings and firings.

The relative quantity of α -Fe₂O₃ was gauged by the intensity of the 104 peak (the strongest α -Fe₂O₃ diffraction) appearing at

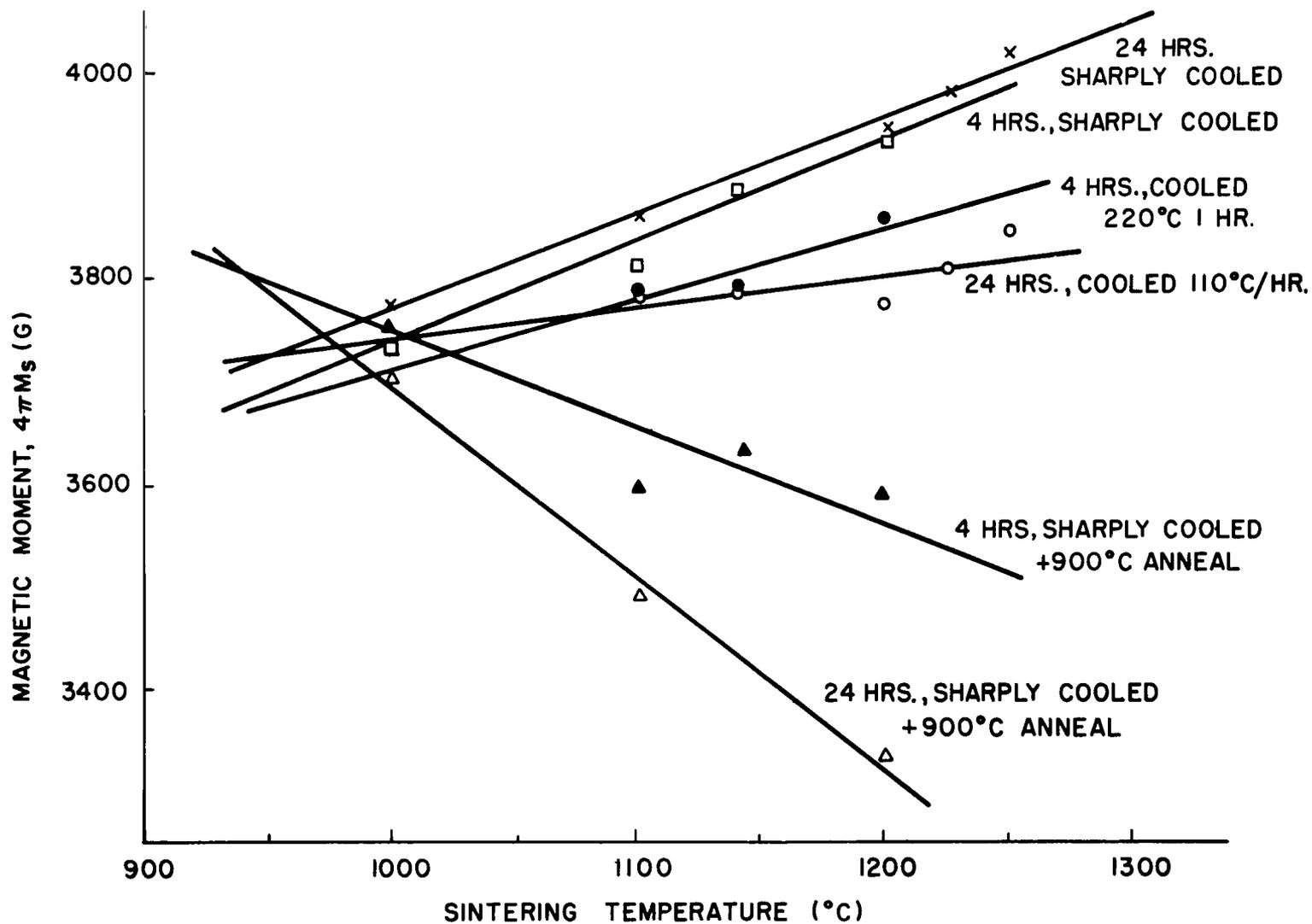


Figure 1.- Effects of sintering temperatures, sintering times, and cooling rate on magnetic moment (density assumed 4.759 g/cm³.)

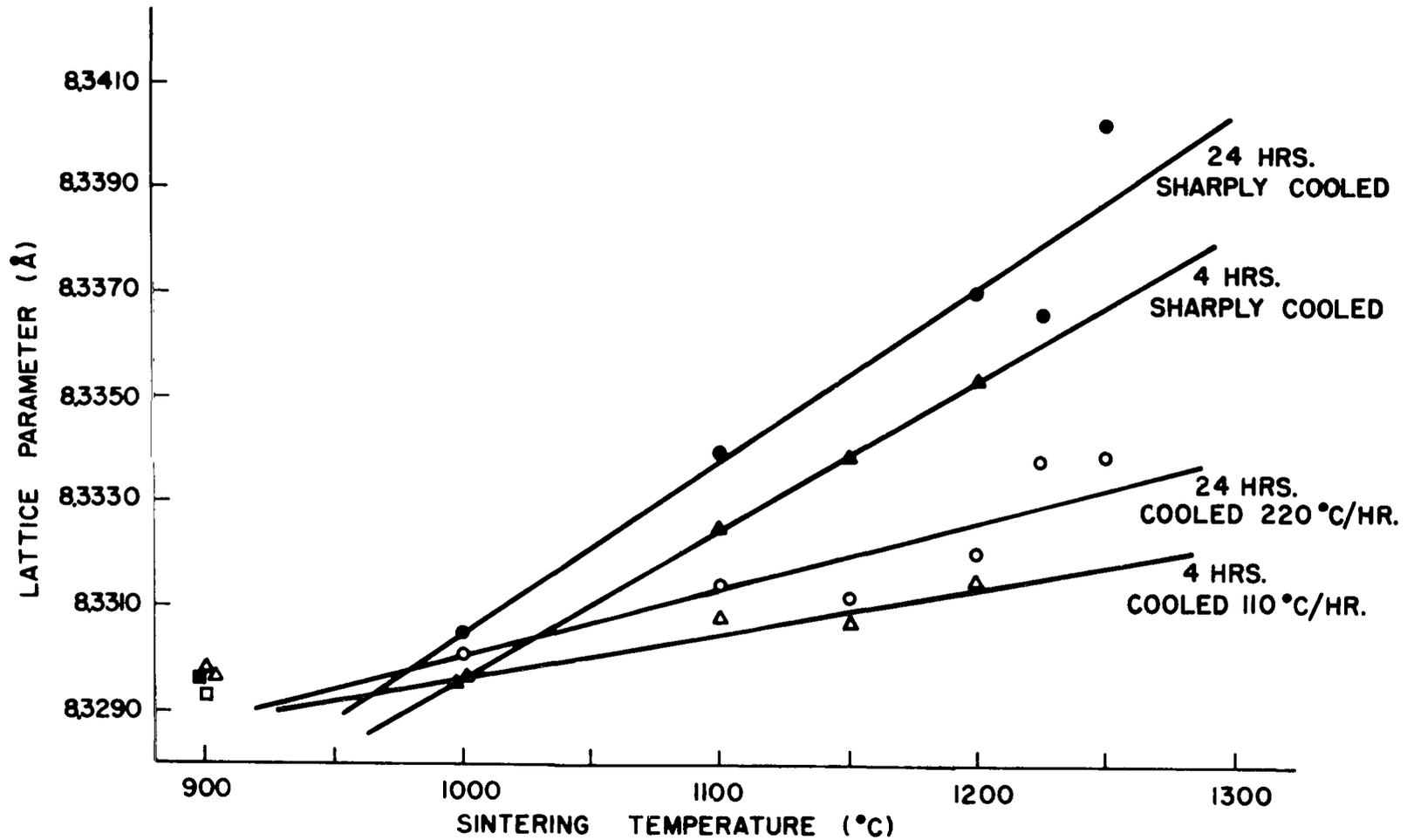


Figure 2.- Effects of sintering temperatures, sintering times, and cooling rates on lattice parameter.

about 33.30 deg 2θ ($d = 2.688 \text{ \AA}$). The height of this peak was zero for the sample fired initially 4 hours at 1000°C, a small bump on the background with 24 hours at 1000°C; it then increased with increasing temperature and time to become more than one-half the height of the 220 peak of the lithium ferrite phase after 24 hours at 1225°C. The x-ray diffraction patterns of all samples, except those fired at temperatures of 1300°C and higher, showed the superlattice peaks associated with the ordering of the lithium on the octahedral sites. The cooling rate of the sharply cooled samples evidently was not sufficiently rapid to achieve lithium disorder; it has been reported (ref. 6) that the cooling must be accomplished in a matter of .1 to 2 seconds to achieve disorder. Little variation in intensity or width of the x-ray diffraction peaks was noted among the various samples and no clear dependence of the intensity or peak width on the cooling rate was evident.

Attempts were made to obtain a disordered sample by quenching a portion of one of the 4-hour-1000°C samples into water from 800°C. The lattice parameter found was 8.3314 \AA and the moment found was 3758 G. Since no large change in moment was observed on quenching sharply enough to achieve disorder of the lithium, it appears very unlikely that any significant transfer of lithium to tetrahedral sites occurs in the stoichiometric material. The spinel superlattice peaks (110, 210, 211, 310, etc.) disappeared from the x-ray diffraction pattern; however, the remaining peaks showed no visible changes in intensity or position. A sensitivity to water and water vapor has been reported* for lithium ferrite; however, no appreciable sensitivity was observed in this experiment. The mechanism of any such action by water in its effect on the properties of lithium ferrite is not known. Kato (ref. 6) reports a lattice parameter of 8.3326 \AA for disordered lithium ferrite quenched from 1000°C and 8.3296 \AA for the ordered material. The chemical analysis reported by Kato indicated a lithium deficiency of about 15 percent; however, the analytical procedures for lithium are not the most reliable. The lattice parameter values from NASA-ERC for the stoichiometric material are in good agreement with those of Kato, but an analysis of one of the NASA-ERC 4-hour-1000°C samples (presumed stoichiometric) indicated a lithium deficiency of only 0.6 percent (see below). The electrical resistivity reported by Kato for the ordered material is too high to be consistent with large lithium deficiencies, unless the samples had been slowly cooled. It appears that Kato's materials were much more nearly stoichiometric than indicated. Kato reports a slightly lower resistivity for disordered lithium ferrite than for the ordered material.

*B. Frackiewicz, NASA/ERC, private communication

Efforts were made to achieve disorder in a sample by allowing powder to fall from a furnace (800°C, 1 atmosphere oxygen) upon an inclined aluminum plate with one end resting in liquid nitrogen. The superlattice peaks of the x-ray diffraction pattern were considerably reduced in intensity but not completely to zero.

The effects of cooling rate on the magnetic moment and lattice parameter were investigated in one series in which all samples were fired at 1100°C for 4 hours under 1 atmosphere oxygen, and then subjected to various cooling schedules. The results are tabulated in Table I. The sample designated as 900°C anneal was the sample initially sharply cooled, annealed at 900°C for 8 hours, and then cooled to room temperature at 10°C/hr.

TABLE I
EFFECT OF COOLING RATE ON
MAGNETIC MOMENT AND LATTICE PARAMETER*

Cooling Rate (°C/hr)	Measured Moment [$4\pi M_s$ (G)]	Lattice Parameter (Å)
Sharp	3808	8.332 ₈
320	3767	8.332 ₅
220	3765	8.331 ₁
110	3776	8.330 ₄
100	—	8.330 ₅
20	3748	8.330 ₂
900°C Anneal +10°C/hr	3620 (two phase)	—

*All samples fired 4 hours at 1100°C.

A series of heat treatments was carried out at 1200°C to investigate, to a limited degree, the rate of attainment of the final properties. In this series, samples were heated at times varying from 1 minute to 24 hours, then rapidly cooled by removing the samples from the furnace and allowing them to cool under ambient room conditions. These results are shown in Figure 3. From these data, it appears that the rates of increase of the

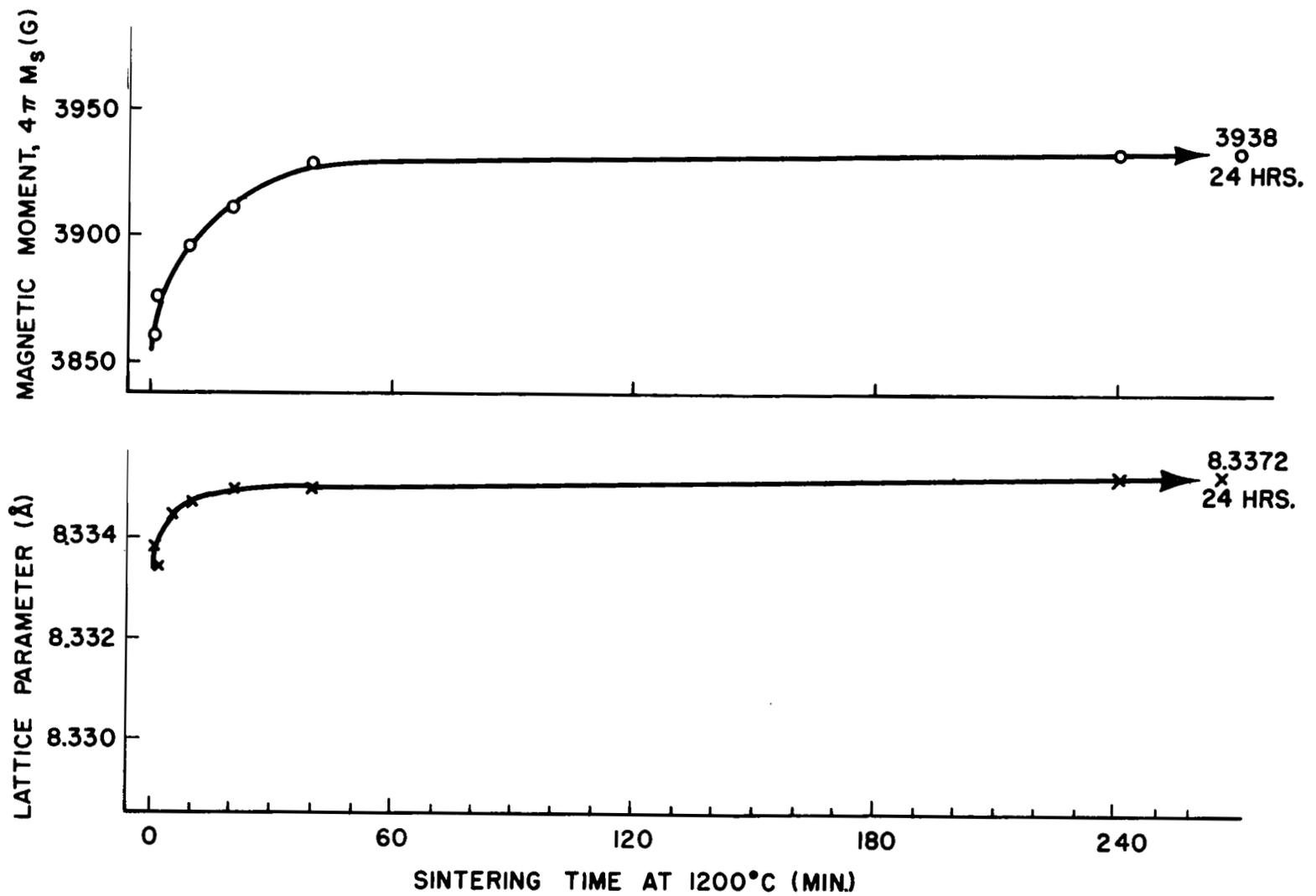


Figure 3.- Effect of time on magnetic moment and lattice parameter at 1200°C, all samples sharply cooled; the 24 hour values are designated at the right for each property.

magnetic moment and the lattice parameter at 1200°C are very large at first, but rapidly decrease with time, becoming nearly stable after about 40 minutes.

The magnetic moments versus lattice parameters for all single-phase materials have been plotted in Figure 4, regardless of the heat treatment. The degree of departure from stoichiometry is presumed to decrease with decreasing temperature down to about 1000°C. The value of the moment at which a straight line through the points intersects the stoichiometric lattice parameter abscissa (8.3293 Å) should be the magnetic moment of stoichiometric lithium ferrite at 25°C. This value, $4\pi M_S = 3732$ G, is well within the experimental error of the values 3725 G for the 4 hour-1000°C material, sharply cooled, and 3747 G for this same material after the 900°C anneal, and essentially equal to the value derived below as the best-fit value for all the data: 3736 G. An independent measurement of the magnetic moment was made on a separately prepared sample by Mee, Besser, and Whitcomb (ref. 17). This sample was fired at 1000°C for 4 hours under 1 atmosphere oxygen, and then cooled rapidly as described above. The moment found at 25°C was 3720 ±40G. This value is also within the experimental error of all the above values, even though the measurements were made by independent workers using a different magnetometer. This same group of workers also obtained a chemical analysis of the sample and found the ratio Fe/Li = 5.03. This corresponds to a lithium deficiency of 0.6 percent; however, this is much less than the experimental analytical error for lithium and must be so regarded in this light.

IV. DISCUSSION

The volatilization of lithium (probably as the oxide) from lithium aluminum oxide has been studied by Hummel, Sastry and Watring (ref. 18), from lithium nickel oxides by Iida (ref. 19), and a lithium nickel ferrite by Salmon and Marcus (ref. 20). It is generally accepted that spinel lithium ferrite shows a similar tendency to lose lithium.

The precipitation of α -Fe₂O₃ during the 900°C annealing treatment is convincing evidence that lithium has been lost from NASA-ERC materials, and the increasing amount of α -Fe₂O₃ with increased sintering temperature suggests that the lithium loss and the increases in magnetic moment and lattice parameter are interrelated. It is clear that stoichiometric lithium ferrite can exist in only those samples which yielded no α -Fe₂O₃ precipitate and also showed no change in moment or lattice parameter, within experimental error, before and after the annealing and slow cooling treatment. Further, it is unlikely that an excess of Li₂O in the structure, if this can occur, would result in a decrease in lattice parameter. Strickler and Roy (ref. 10) found

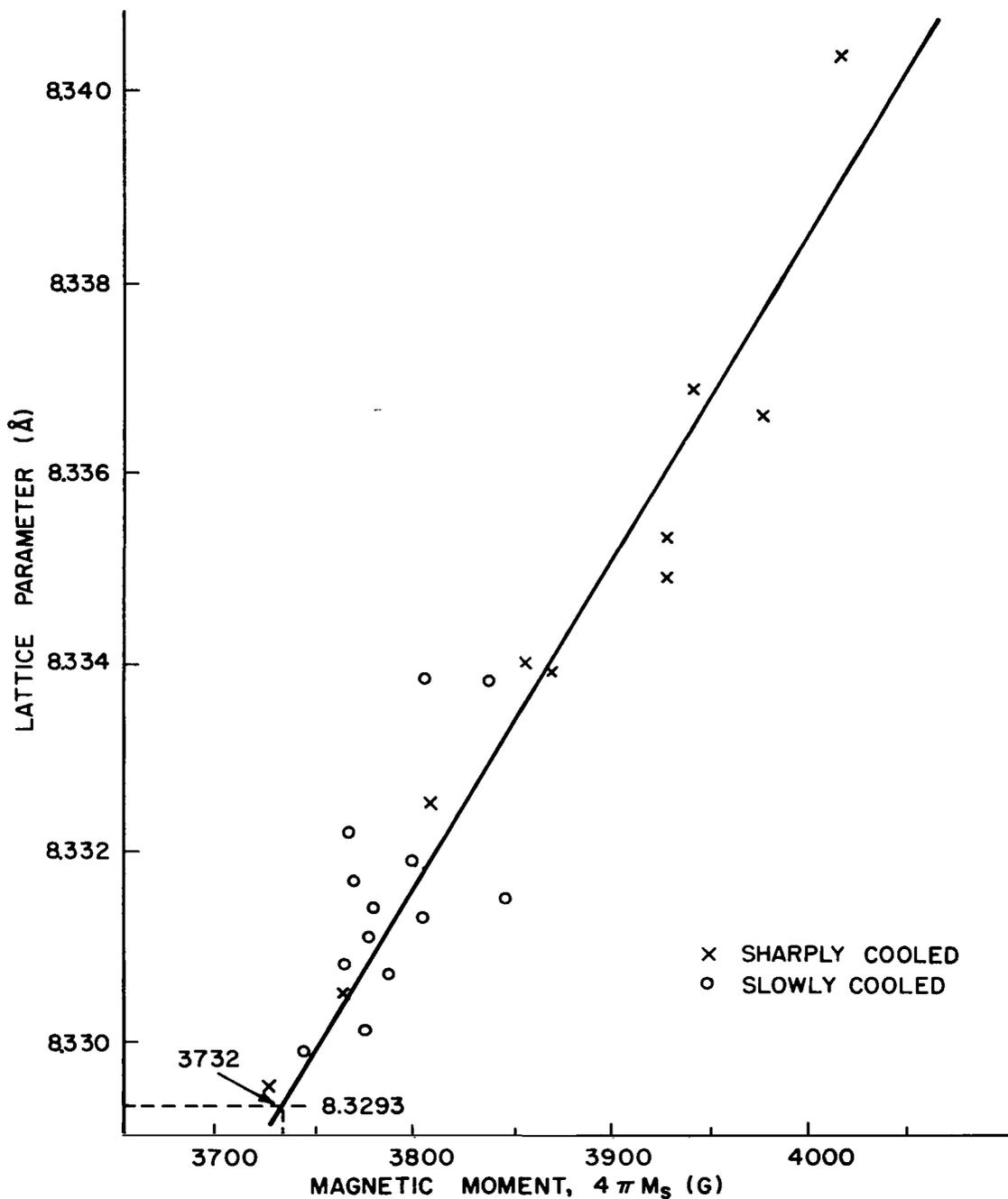


Figure 4.- Magnetic moment versus lattice parameter for all single-phase materials regardless of sintering times or cooling rates; the 8.3293 Å lattice parameter represents the value derived as the lattice parameter for stoichiometric $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$, and the intersection of the curve with this abscissa yields the corresponding magnetic moment: 3732 G.

no evidence that $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ does dissolve LiFeO_2 ; this would be equivalent to excess lithium in the structure. Thus, the material yielding the minimum lattice parameter should be the one most closely approaching stoichiometric lithium ferrite. Above this temperature, lithium-deficient materials will result which will give magnetic moments which are either too high or too low depending upon the cooling rate, as shown in Figure 1. That magnetic moment and lattice parameter values very near the stoichiometric values have been obtained is no guarantee that the material is stoichiometric, since any intermediate value of the moment can be obtained by a proper choice of cooling rate. The lattice parameter would not necessarily differ greatly from the stoichiometric value in this case.

All materials fired at 900°C and no higher and the materials fired only 4 hours at 1000°C , whether rapidly cooled, slowly cooled, or annealed and very slowly cooled, showed lattice parameters within the estimated experimental error of the average value, 8.3296 \AA . This can be assumed to approach closely the lattice parameter of stoichiometric lithium ferrite, $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$, subject only to the condition that lithium ferrite will accept the full quota of lithium. There is no reason for believing that it will not. The true magnetic moment of stoichiometric lithium ferrite cannot be so directly and reliably derived. A non-ferromagnetic material, when present as a second phase or impurity, such as $\alpha\text{-Fe}_2\text{O}_3$, Li_2O or Li_2CO_3 , will reduce the measured moment and prevent a direct measurement of the true moment. Because of the significant magnitude of the detectability limit of the NASA-ERC x-ray diffraction methods, there is no guarantee of the complete absence of these contaminants and, therefore, no assurance that the value obtained from an individual moment measurement is the true moment. The magnetic moments obtained for the various 4-hour- 1000°C firings indicate the stoichiometric moment to be near 3735 G. The six curves of Figure 1 show a minimum divergence at about 900°C . The average of the moments along this ordinate is only slightly smaller than this value; however, this value is not highly reliable.

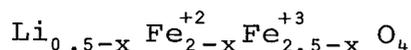
If all moments are plotted versus the corresponding lattice parameters (Figure 4), a curve of much greater point density is obtained. The best-fit or least-squares line through the collection of points should pass through the intersection of the stoichiometric moment ordinate and the stoichiometric lattice parameter abscissa, 8.3293 \AA , the value found to be the probable lattice parameter of stoichiometric lithium ferrite (see below). The magnetic moment thus derived is found to be 3732 G, which is very close to the average of the individual measurements for the 4-hour- 1000°C firings.

Strickler and Roy (ref. 10) state that the equilibrium oxygen pressure over lithium ferrite reaches 1 atmosphere below

1000°C. The oxygen loss associated with this process and with the Li₂O volatilization is not expected to generate any appreciable number of oxygen vacancies in the lattice since the binary oxides of iron show no such tendency. All such binary oxides of iron have close-packed oxygen sublattices, the variations in composition being achieved by changes in the valence state and packing density of iron. To understand the temperature-induced variations in the properties of lithium ferrite, cognizance must be taken of this fact and of the loss of lithium.

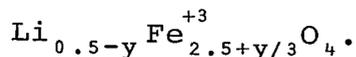
From the above, two limiting cases can now be derived:

(1) those materials which are rapidly cooled under lower oxygen pressures, and (2) those materials which are slowly cooled under higher oxygen pressures. In both cases, when lithium is removed from a region of the crystal, from a selected unit cell, for example, and if that unit cell retains its full complement of 32 oxygens, the positive charge of the departed lithium must be made up in some manner. This is accomplished by the diffusion of iron into the crystal from the surface as the oxygen on the surface is removed. In the first case, applicable to rapidly cooled materials and low oxygen pressures, each vacated lithium site is reoccupied, in effect, by an Fe⁺² ion diffusing in from the crystal surface. Charge neutrality is maintained by the concurrent reduction of another Fe⁺³ to Fe⁺². The phase composition can now be represented:



This formulation can be viewed as representing a solid solution between spinel lithium ferrite and Fe₃O₄. With few exceptions, the Fe⁺² ions should be found on octahedral sites, as in the case of Fe₃O₄.

The second limiting case is applicable to lithium loss not correlated with an oxygen evolution and reduction of Fe⁺³ to Fe⁺². In the limit the additional ions diffusing in will be Fe⁺³ with only one-third the vacated lithium sites so occupied. The composition of the phase can be formulated:



This picture can also be viewed as a solid solution between spinel lithium ferrite and γ-Fe₂O₃, but, since γ-Fe₂O₃ is unstable with respect to the alpha form at these temperatures, materials deficient in lithium might be expected to show this instability to some degree under strong oxidizing conditions and dissociate into a higher lithium-content phase (spinel) and α-Fe₂O₃.

According to the above pictures, the population of the octahedral sites by magnetic cations has been increased and an increase in the measured magnetic moment should be found. It is assumed to be true that the tetrahedral site cations and the octahedral site cations generate separate magnetic sublattices which are opposed in a Neel-type configuration.

Following the above descriptions, one can calculate the lithium loss from the magnetic moment and lattice parameter increases. One method would be to consider the individual samples to be solid solutions of the end members of the series, lithium ferrite and Fe_3O_4 in the first limiting case and lithium ferrite and $\gamma\text{-Fe}_2\text{O}_3$ in the second. An interpolation technique (Vegard's law) would be used with the lattice parameters. These require that dependable values be available for the magnetic moments and lattice parameters of the end members. Such values were not found after limited effort, except for the lattice parameters of Fe_3O_4 and lithium ferrite and the magnetic moment of lithium ferrite (the latter two from this study, which we assume to be good values). Abrahams and Calhoun (ref. 21) and Tombs and Rooksby (ref. 22) report the same value of $8.3940 \pm 0.0005 \text{ \AA}$ for the lattice parameter of Fe_3O_4 at 22°C . By use of a thermal expansion coefficient provided by the former authors, a value of 8.3944 \AA is obtained at 28°C , the temperature of the NASA-ERC measurements.

Another method is available for the calculation of lithium losses and was preferred to the procedure above. This method involves relating the measured magnetic moment of a particular lithium oxide deficient sample, either with or without separate oxygen loss, to these deficiencies through the proportionate change in the theoretical number of Bohr magnetons per unit weight or per unit volume. To obtain values on a volume basis, it is necessary to include a density correction which is expressed in terms of the deficiencies and the measured lattice parameters. These values, however, will not be completely independent of those derived by the Vegard's law approach. Thus, the emphasis was placed on calculation from the proportionate change in the number of Bohr magnetons per unit weight. Separate values of lithium loss were calculated by this method and by the Vegard's law method for the limiting case of the rapidly cooled samples. The results are tabulated in Table II. The details of the calculation procedure are given in Appendix A.

It should be pointed out here that two different values can be derived to express the degree of lithium volatilization: (1) a lithium loss value, and (2) a lithium deficiency value. The former represents the percentage of the original quantity of lithium volatilized; this is not equal to the lithium deficiency of the final product. The lithium deficiency represents the

TABLE II

DATA CORRESPONDENCE IN FIRST LIMITING CASE FOR SHARPLY COOLED MATERIALS

Sintering Conditions	Calcd. Li Loss (%)			Calcd. Li Def. (%)	Magnetic Moments [$4\pi M_s$ (G)]		Lattice Parameters (Å)		Density Calcd. (g/cm ³)
	From Moment	From Lat. Par.	Ave.		Measd.	Calcd. From Ave.	Measd.	Calcd. From Ave.	
4 hrs., 1000°C	-	-	-	-*	3725	-	8.329 ₅	-	4.759
24 hrs., 1000°C	2.2	2.2	2.2	1.9	3769	3769	8.330 ₅	8.330 ₅	4.767
4 hrs., 1100°C	4.8	5.8	5.3	4.4	3808	3816	8.332 ₅	8.332 ₂	4.779
24 hrs., 1100°C	8.0	8.5	8.3	7.0	3857	3861	8.334 ₀	8.334 ₀	4.790
4 hrs., 1150°C	8.7	8.4	8.6	7.2	3868	3865	8.333 ₉	8.334 ₀	4.792
4 hrs., 1200°C	12.7	11.0	11.9	10.1**	3928	3915	8.335 ₄	8.335 ₉	4.804
24 hrs., 1200°C	13.5	13.7	13.6	11.6	3941	3942	8.336 ₉	8.336 ₉	4.811
24 hrs., 1225°C	15.8	13.3	14.6	12.4	3975	3957	8.336 ₇	8.337 ₄	4.815
24 hrs., 1250°C	18.4	19.6	19.0	16.3	4015	4025	8.340 ₃	8.339 ₉	4.832

*Analyzed 0.6%

**Analyzed 9.2%

percentage of the lattice sites originally occupied by lithium but occupied in the final product by Fe^{+2} or Fe^{+3} . (It cannot be stated that the lithium site is occupied, in particular, by either valence state.) These definitions are followed throughout this report. In the rapid-cool case, the fractional lithium deficiency will be $5p/6-p$, where p is the fractional lithium loss (see Appendix C).

In Table II, the first column gives the temperature at which the samples were sintered and the time at temperature. The next three columns give the calculated lithium losses: column 2 lists values computed from the measured moments (column 6); column 3 lists the values computed from measured lattice parameters (column 8), assuming Vegard's law; and column 4 shows the average of the two loss values. These average lithium losses were used to calculate the magnetic moments and lattice parameters given in columns 7 and 9 and to calculate the densities of column 10. The lithium deficiencies of column 5 were derived from the average losses as described above.

Both the calculated and measured moments of columns 6 and 7 of Table II are uncorrected for the density changes accompanying the oxygen and lithium losses and, therefore, are proportional to the magnetic moment per gram. Dividing these values by $4\pi d$ ($d = 4.759 \text{ g/cm}^3$, the x-ray density of stoichiometric lithium ferrite assuming the lattice parameter $a = 8.3293 \text{ \AA}$) yields the magnetic moments in emu/g. The stoichiometric material is generally the one sought and these values are those which would be obtained under the given sintering conditions if the product were assumed stoichiometric and the corresponding density applied.

The experimental data were analyzed as follows: values for the magnetic moment and lattice parameter of stoichiometric lithium ferrite and the lattice parameter of magnetite were determined (see Appendix A) in a manner consistent with a best least-squares fit to the data where the magnetic moment and lattice parameter data were weighted relative to the respective estimated errors. The resulting values are 3736G and 8.3293 Å for the moment and lattice parameter of lithium ferrite and 8.3943 Å for the lattice parameter of magnetite. It should be noted that a change of one unit in the least significant figure of either or both lithium ferrite values produces a change of one or more units in the next-to-least significant figure of the best-fit magnetite lattice parameter value. The lattice parameter of lithium ferrite (8.3293 Å) which gives the best fit to all the data is also the value obtained from the 4-hour-1000°C sintering with the silicon internal standard technique. The best-fit magnetic moment value differs much less than the experimental error from the values derived graphically above and from the average of the values obtained by direct measurement of the 4-hour-1000°C samples.

The lithium loss as a function of the sintering temperature for sintering times of 4 and 24 hours is plotted in Figure 5. Straight lines have been drawn through the points, although there is no assurance that lithium loss need be a linear function of temperature. Indeed, with greater lithium losses and high temperatures, deviation from linear might very well be expected. These curves indicate that the lithium loss at any selected temperature and the temperature at which lithium loss begins is a function of sintering time. Since the approach of the curves to the axis is very likely non-linear, the temperature at which volatilization begins need not be assumed to be time-dependent. It is more probable that these intercepts merely suggest the relative rates of loss, and signal the onset of rapid increases in the lithium volatilization rates. In general, some time-dependence of lithium loss would be expected.

Samples were also fired at 1300 and 1400°C, but no dependable calculations of lithium loss could be made. The peaks of the x-ray diffraction patterns were considerably smaller and broader and did not permit the determination of accurate lattice parameters. The peaks of α -Fe₂O₃ were pronounced in both cases, indicating a two-phase material, which rendered the magnetic moment data unusable. The measured moments were considerably lower than the stoichiometric value, as would be expected.

Calculations of lithium deficiencies on the basis of the change in the number of Bohr magnetons per unit volume, using densities expressed in terms of the deficiencies and the measured lattice parameters, yielded values differing by only a few hundredths in percentage from the lithium deficiencies derived from the loss values calculated on the basis of the change in Bohr magnetons per unit weight.

Mee, Besser, and Whitcomb (ref. 17) also analyzed one lithium-deficient material (4 hours, 1200°C + 900°C anneal). The analysis showed 9.2 ±2.7 percent lithium deficiency; the NASA-ERC calculated value is 10.1 percent (11.86 percent lithium loss). The difference between the analyzed and calculated values is equivalent to an analysis error of only about 1 percent. The apparently large error quoted for the analysis value represents an analysis error of only 3 percent. The agreement between these two values is surprisingly good and, when considered in conjunction with the analysis results quoted above for a stoichiometric material, suggest that the analysis may be more accurate than quoted.

A similar series of calculations for the materials cooled at moderately slow rates require modification. The 900°C anneal results suggest that precipitation of α -Fe₂O₃ probably has started, but has not proceeded to a point that α -Fe₂O₃ peaks appear in the x-ray diffraction patterns. The view here is that the products

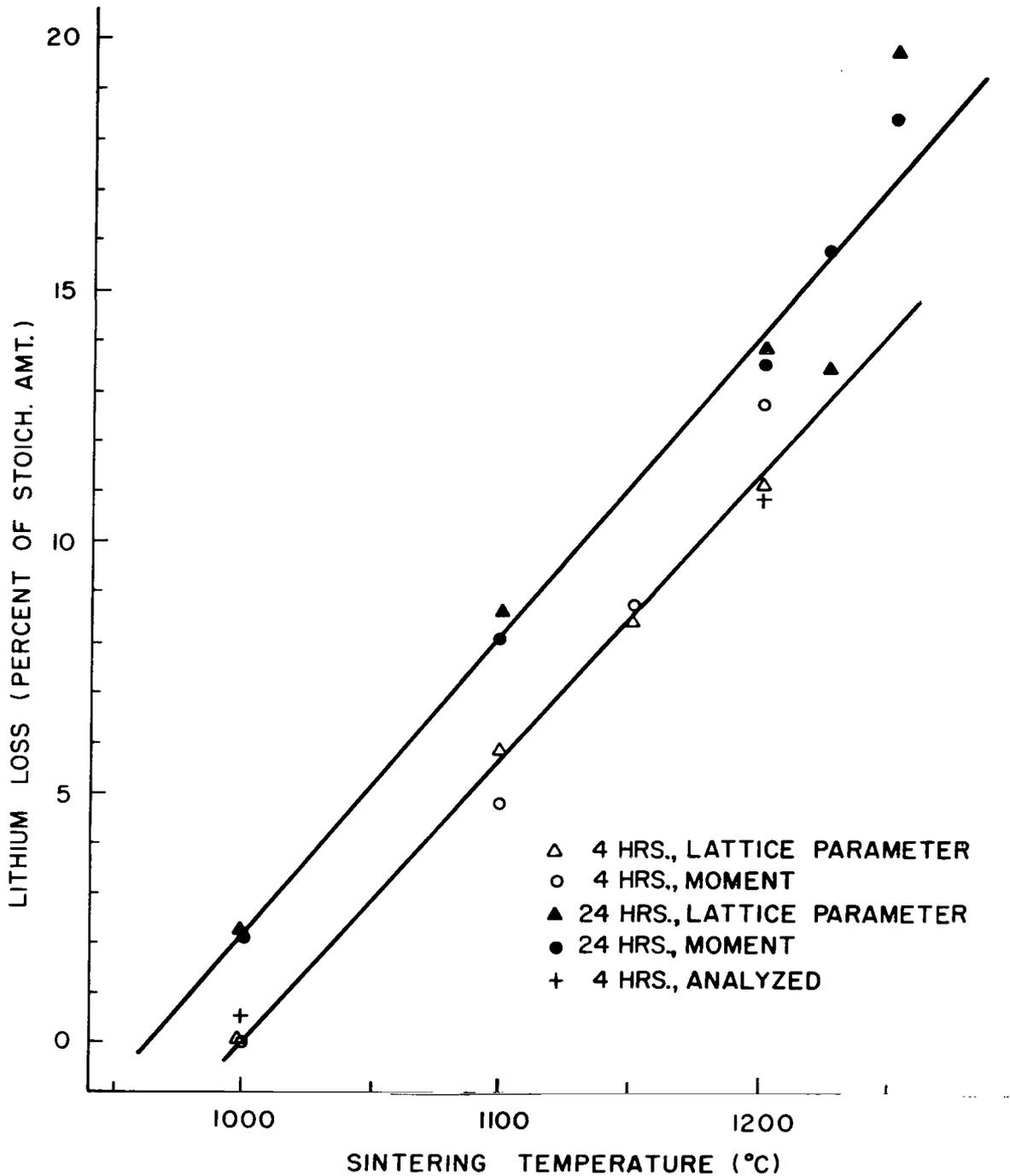


Figure 5.- Calculated lithium loss as a function of sintering temperature; values of lithium are differentiated according to time at temperature and basis for calculation.

can be described as a mixture of a lithium ferrite phase with dissolved $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ precipitate. This modified calculation procedure is included in Appendix B and the results are presented in Table III. The lithium loss was assumed to be the average value computed for the corresponding rapidly cooled materials (column 4, Table II). As Figure 3 shows, any additional lithium loss occurring during the cooling process should be small. The results of this calculation serve to indicate that the materials probably approach the state assumed. Attempts to calculate lithium losses directly without providing for the presence of $\alpha\text{-Fe}_2\text{O}_3$ as a second phase yielded values completely inconsistent with the rapid-cool results.

The percentage of the slowly cooled products estimated to be $\alpha\text{-Fe}_2\text{O}_3$ (column 8) is of the order generally considered to be the lower limit of detectability of a second phase by standard x-ray diffraction techniques. The detectability of the $\alpha\text{-Fe}_2\text{O}_3$ is further reduced if it is present in very fine or submicroscopic particle size. The $\alpha\text{-Fe}_2\text{O}_3$ precipitated after the 900°C anneal was detected in all cases, including the 24-hour- 1000°C sample, but not the 4-hour- 1000°C sample. The fact that such amounts of $\alpha\text{-Fe}_2\text{O}_3$ were detected after the anneal, but larger calculated amounts in the slow-cooled materials were not may be either a result of better coagulation of the $\alpha\text{-Fe}_2\text{O}_3$ or errors in the calculated values. This apparent discrepancy is not considered significant.

In columns 5 and 6 are shown the magnetic moments (without density correction) derived for the magnetic lithium ferrite phases present in the products. Column 5 shows the value obtained from the magnetic moment, applying the lithium loss values of column 4, Table II, and the fractional Fe_2O_3 precipitation value of column 7, Table III. Column 6 shows the moments derived by calculating a lithium deficiency for the lithium ferrite phase from the lattice parameters. The agreement is very satisfactory. A first-order reaction rate for the precipitation process (instantaneous rate dependent upon the concentration of excess Fe_2O_3 dissolved) would require that the fraction of Fe_2O_3 precipitated be constant if the annealing time and cooling rates were identical. The values of column 7 show reasonably good constancy in most cases and are generally satisfactory, in view of the experimental errors and the indirect manner of derivation.

The value derived for the lattice parameter of $\gamma\text{-Fe}_2\text{O}_3$ corresponding to the best-fit of the data was 8.357 \AA . Haul and Schoon (ref. 23) report a lattice parameter of 8.350 \AA for $\gamma\text{-Fe}_2\text{O}_3$ prepared by an electric arc process, and a value of 8.338 \AA for a material prepared by oxidation of Fe_3O_4 . Van Oosterhout and Rooijmans (ref. 24) and Schrader and Büttner (ref. 25) report that $\gamma\text{-Fe}_2\text{O}_3$ is tetragonal with the lattice parameter $a = 8.33 \text{ \AA}$ and

TABLE III

DATA CORRESPONDENCE IN SECOND LIMITING CASE FOR SLOWLY COOLED MATERIALS

Sintering and Cooling Conditions	Li Loss % Original	Lattice Parameter Measd. (Å)	Magnetic Moment [$4\pi M_s$ (G)]			Fe ₂ O ₃ Precipitated	
			Measd. Total	Calcd. (Magn. Phase)		Fraction of Excess	Wt. % of Sample
				From M	From a _o		
24 hrs., 1000°C, 80°C/hr	2.2	8.330 ₀	3702	3746	3755	0.57	1.2
4 hrs., 1100°C, 110°C/hr	5.3	8.330 ₁	3769	3787	3778	0.10	0.5
24 hrs., 1100°C, 110°C/hr	8.3	8.331 ₁	3777	3815	3812	0.12	1.0
4 hrs., 1150°C, 220°C/hr	8.6	8.330 ₇	3787	3819	3806	0.10	0.8
4 hrs., 1200°C, 220°C/hr	11.9	8.331 ₅	3747	3839	3833	0.21	2.4
24 hrs., 1200°C, 110°C/hr	13.6	8.331 ₇	3769	3859	3847	0.18	2.4
24 hrs., 1225°C, 110°C/hr	14.6	8.333 ₇	3802	3874	3895	0.13	1.8
24 hrs., 1250°C, 110°C/hr	19.0	8.334 ₀	3838	3921	3924	0.11	2.0
4 hrs., 1000°C, Rapid Cool +8 hrs., 900°C, 10°C/hr	-	8.329 ₇	3748	-	-	-	-
24 hrs., 1000°C, Rapid Cool +8 hrs., 900°C, 10°C/hr	2.2	8.329 ₉	3693	3744	3752	0.67	1.4
4 hrs., 1100°C, Rapid Cool +8 hrs., 900°C, 10°C/hr	5.3	8.330 ₄	3594	3743	3762	0.87	4.5
24 hrs., 1100°C, Rapid Cool +8 hrs., 900°C, 10°C/hr	8.3	8.330 ₀	3490	3744	3755	0.89	7.1
4 hrs., 1150°C, Rapid Cool +8 hrs., 900°C, 10°C/hr	8.6	8.330 ₃	3631	3786	3781	0.49	4.1
4 hrs., 1200°C, Rapid Cool +8 hrs., 900°C, 10°C/hr	11.9	8.330 ₇	3588	3811	3802	0.48	5.5
24 hrs., 1200°C, Rapid Cool +8 hrs., 900°C, 10°C/hr	13.6	8.330 ₄	3328	3757	3769	0.87	11.5

$c/a = 3.000$. The latter authors find that the cation vacancies order along a screw axis parallel to the tetragonal c -axis. It is possible that the two values reported by Haul and Schoon represent different degrees of order or partial reduction. Either could occur in an electric arc. The smaller value is to be preferred as the lattice parameter of $\gamma\text{-Fe}_2\text{O}_3$. Any such vacancies occurring in lithium ferrite are disordered, and it is not unlikely that such materials with disordered vacancies would have a larger lattice parameter. A small increase in lattice parameter was noted on disordering of stoichiometric lithium ferrite. Here ions of comparable size are exchanging positions rather than ions with vacancies, and a somewhat greater effect might well be expected in the latter case. The NASA-ERC value of 8.357 \AA for the lattice parameter for $\gamma\text{-Fe}_2\text{O}_3$ agrees sufficiently well, in view of the manner of derivation, that measure of support is given to the NASA-ERC interpretation.

There were indications that the precipitation of $\alpha\text{-Fe}_2\text{O}_3$ from the lithium-deficient materials after the 900°C anneal was not complete in that the amount precipitated was not directly proportional to the lithium losses calculated (column 4, Table II). The relative amount of $\alpha\text{-Fe}_2\text{O}_3$ appearing as a second phase can be estimated experimentally from the intensity of the strongest $\alpha\text{-Fe}_2\text{O}_3$ peak found in the x-ray diffraction pattern and normalizing to the intensity of the spinel 220 peak. The intensity of the spinel 220 peak is derived essentially only from the tetrahedral site ions and should not be appreciably affected by moderate amounts of lithium deficiency. Plots of the reduced intensity of the $\alpha\text{-Fe}_2\text{O}_3$ peak (I_α/I_{220}) versus calculated lithium losses and versus the sintering temperature were far from linear. Plots of reduced intensity versus the calculated amount of $\alpha\text{-Fe}_2\text{O}_3$ precipitated showed much more linear behavior (Figure 6), giving further measure of support to the NASA-ERC assumptions.

The question arises as to whether the changes in the magnetic moment and lattice parameter could be the result of exchange of sites by octahedral lithium and tetrahedral iron, either as the sole effect or in combination with a loss of lithium and oxygen and reoccupation of the lithium sites by iron. The precipitation of $\alpha\text{-Fe}_2\text{O}_3$ after the anneal at 900°C establishes that lithium oxide has been lost and places a minimum value on the extent of this loss. The amount of $\alpha\text{-Fe}_2\text{O}_3$ precipitated, as calculated from the moments and lattice parameters, correlated well with the lithium loss calculated in the higher lithium losses cases. The effects on the moment and lattice parameter by any site exchange by lithium must then be confined to the differences between the observed values and the values which would be derived on the basis of the amount of $\alpha\text{-Fe}_2\text{O}_3$ actually precipitated. The latter was not directly determined quantitatively. Chemical analysis results indicate that the differences should be small.

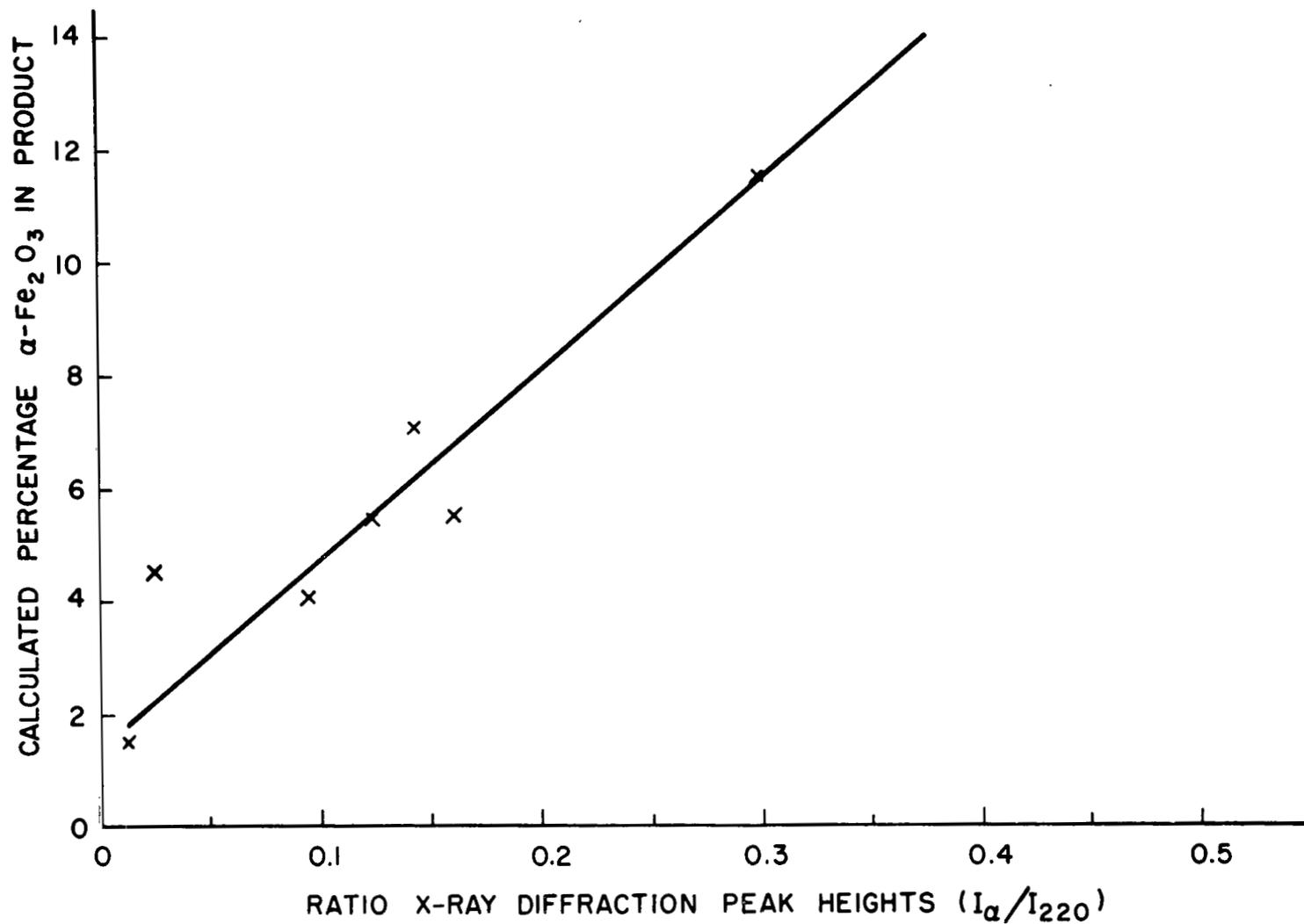


Figure 6.- Calculated percentage of α -Fe₂O₃ present as a precipitate in the products after the 900°C anneal versus the height of the strongest α -Fe₂O₃ diffraction peak normalized to the height of the 220 peak of the lithium ferrite component (I_{α}/I_{220}).

The magnetic moment is very sensitive to any exchange of sites by lithium with tetrahedral iron. The lithium losses calculated above from magnetic moments and from lattice parameters agreed well within the limits of experimental error. Thus, any other mechanism proposed to account for the observed moment and lattice parameter increases, such as site exchange by octahedral lithium with tetrahedral iron, must show that some relative effect on those properties in order that a comparable degree of correlation be obtained. For the lithium loss mechanism described above, a 25 percent lithium deficiency in the final product should yield a moment increase of 15 percent and a lattice parameter increase of about 0.016 Å; a shift of the same number of lithiums to tetrahedral sites should cause a moment increase of 50 percent, which would require a lattice expansion of about 0.053 Å to retain the same degree of correlation. A consideration of the ionic radii of Li^+ and Fe^{+3} suggests that this is reasonable. There is, therefore, no assurance that site exchanges of considerable magnitude could be established on this basis and even less in the case of small amounts, which would necessarily be the case here.

A careful study of the various structural factors which generate certain x-ray diffraction peaks indicates that the peaks most sensitive to site exchanges are those arising from the 111, 210, and 222 planes. Disorder within the octahedral sites alone would cause large changes in the intensity of the 210 peak; therefore, this peak must be eliminated from consideration. Both the 111 and 222 peaks represent cases in which the phase and scattering amplitudes of the various intensity contributions are such as to result in almost complete cancellation. A small change in any one of the contributions can thus have a relatively strong effect on resultant intensity. It has already been established that considerable lithium loss must occur. The effect on the intensity of these peaks arising from the replacement of lithium on the octahedral sites by iron without altering the tetrahedral population (lithium loss) is in the same direction as with site exchange but somewhat less in degree. One is thus restricted to differentiating between the changes in intensity resulting from the two processes, with the intensity change being small in each case. Unfortunately the normal statistical fluctuations encountered in x-ray scanning techniques are such as to render such attempts impractical. Accurate intensities measurements might succeed in clarifying this point.

The difficulty which was experienced at NASA-ERC in attempting to achieve octahedral disorder in lithium ferrite is consistent with the observations of Kato (ref. 6), and reflects the high value of the octahedral site ordering energy calculated by de Boer, van Santen and Verwey (ref. 3). The energy associated with the shift of lithium between octahedral and tetrahedral sites must certainly be greater than the energy of octahedral

site ordering. All materials investigated which were slowly-cooled or sharply cooled from temperatures of 1250°C and below showed well developed superlattice peaks. In view of this, there appears to be little basis for assuming any large octahedral-tetrahedral site shift by lithium. A limited amount is possible and may occur on a sharp quench of non-stoichiometric materials. The small moment increase observed in the NASA-ERC single quench into water of a stoichiometric sample is within experimental error and indicates that any shift of lithium to tetrahedral sites is very small at most.

Electronics Research Center
National Aeronautics and Space Administration
Cambridge, Massachusetts, December 1968
129-03-15-03-25

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APPENDIX A

The fractional lithium loss, p , can be calculated from the measured magnetic moments (in emu/g) as follows: each gram-formula ($\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$) weight of stoichiometric lithium ferrite, A_s , dissociates into a product composed, in effect, of $(1-p)A_s$ grams of stoichiometric lithium ferrite and $(5/6)pA_m$ grams of Fe_3O_4 . The magnetic moment per gram of this product, σ_p , will be

$$\sigma_p = \frac{(1-p)A_s\sigma_s + (5/6)pA_m\sigma_m}{(1-p)A_s + (5/6)pA_m} \quad (\text{A-1})$$

where σ_s and σ_m are the magnetic moments in emu/g of stoichiometric lithium ferrite and Fe_3O_4 , respectively. For σ_m a value is used derived in accordance with the scheme of the proportionate increase in the number of Bohr magnetons over that of lithium ferrite following the mechanism of the first limiting case described above:

$$\sigma_m = \left[\frac{\left(\frac{32\mu_B/\text{unit cell of Fe}_3\text{O}_4}{8A_m/\text{unit cell of Fe}_3\text{O}_4} \right)}{\left(\frac{20\mu_B/\text{unit cell of Li}_{0.5}\text{Fe}_{2.5}\text{O}_4}{8A_s/\text{unit cell of Li}_{0.5}\text{Fe}_{2.5}\text{O}_4} \right)} \right] \sigma_s \quad (\text{A-2})$$

$$\sigma_m = 8A_s\sigma_s/5A_m \quad (\text{A-3})$$

Substituting in Eq. (A-1) yields:

$$\sigma_p = \left[\frac{(1-p)A_s\sigma_s + (5/6)pA_m(8A_s\sigma_s/5A_m)}{(1-p)A_s + (5/6)pA_m} \right] = \left[\frac{(1 + p/3)\sigma_s}{1 - 0.0683p} \right], \quad (\text{A-4})$$

and rearranging gives:

$$p = \frac{\sigma_p - \sigma_s}{0.0683 + \sigma_s/3} \quad (\text{A-5})$$

APPENDIX B

For the second limiting case, applicable to strongly oxidizing conditions, as described in the Discussion (page 13) one may assume one gram-formula weight of $\text{Li}_{0.5}\text{O}_4$ to dissociate forming $(1-p)A_s$ grams of $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ and, in effect, $(5/4)pA_h$ grams of Fe_2O_3 . Here A_h represents the gram-formula weight of Fe_2O_3 and the other symbols have the same significance as above. It is also assumed that of the Fe_2O_3 formed during the dissociation, a fraction, f , remains dissolved and $(1-f)$ precipitates as $\alpha\text{-Fe}_2\text{O}_3$. The $\alpha\text{-Fe}_2\text{O}_3$ contribution to the total measured moment will be insignificant. Thus, the magnetic moment in emu/g of the mixed product, σ_p , will be:

$$\sigma_p = \frac{(1-p)A_s\sigma_s + (5/4)pfA_h\sigma_g}{(1-p)A_s + (5/4)pfA_h + (5/4)p(1-f)A_h} \quad (\text{B-1})$$

where σ_g is the magnetic moment per gram of $\gamma\text{-Fe}_2\text{O}_3$. To express σ_g in terms of a proportionate increase in the theoretical number of Bohr magnetons per unit weight relative to that of lithium ferrite following the second limiting case mechanism described above, the following equation is used:

$$\sigma_g = \left[\frac{\left(\frac{(26 \frac{2}{3}\mu_B)/\text{unit cell of } \gamma\text{-Fe}_2\text{O}_3}{(10 \frac{2}{3}A_h)/\text{unit cell of } \gamma\text{-Fe}_2\text{O}_3} \right)}{\left(\frac{20\mu_B/\text{unit cell of } \text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4}{8A_s/\text{unit cell of } \text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4} \right)} \right] \sigma_s \quad (\text{B-2})$$

$$\sigma_g = (A_s/A_h)\sigma_s \quad (\text{B-3})$$

Substituting in Eq. (B-1) yields:

$$\sigma_p = \frac{[1-p + (5/4)pf]\sigma_s}{1-p + (5/4)p(A_h/A_s)} \quad (\text{B-4})$$

and rearranging gives:

$$f = \frac{(1-p)(\sigma_p - \sigma_s) + (5/4)p(A_h/A_s)\sigma_p}{(5/4)p\sigma_s} \quad (\text{B-5})$$

APPENDIX C

The relationship between the fraction of the original lithium lost and the fractional lithium deficiency of the final product (first limiting case) was derived as follows: C unit cells of stoichiometric $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ dissociate to generate $(1-p)C$ unit cells of lithium ferrite in which are dissolved $5Cp/6$ unit cells of Fe_3O_4 , where p is the fractional lithium loss as calculated in appendix A. The total number of spinel unit cells generated are

$$(1 - p + 5p/6)C = (1 - p/6)C . \quad (\text{C-1})$$

In each lithium ferrite unit cell there are four lithium sites. The total number of lithium sites in the final product becomes $4(1 - p/6)C$. The total number of the original lithium sites occupied by lithium in the final product is $4(1 - p)C$. The total deficiency of lithium in the product becomes

$$4(1 - p/6)C - 4(1 - p)C = 4(5p/6)C . \quad (\text{C-2})$$

The fractional lithium deficiency is thus:

$$\frac{4(5/6)pC}{4(1 - p/6)C} = \frac{5p}{6 - p} . \quad (\text{C-3})$$

EFFECTS OF LITHIUM AND OXYGEN LOSSES
ON THE MAGNETIC AND CRYSTALLOGRAPHIC PROPERTIES
OF SPINEL LITHIUM FERRITE

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ABSTRACT

A study of the effects of sintering temperatures and cooling rates on the magnetic and crystallographic properties of spinel lithium ferrite shows that both the magnetic moment and lattice parameter increase with sintering temperature. Either annealing at lower temperatures or slow-cooling under oxygen causes re-oxidation of the Fe^{+2} formed at higher temperatures with attendant decreases in moment and lattice parameter and gradual precipitation of $\alpha\text{-Fe}_2\text{O}_3$ as a second phase. The various products formed have been shown to be equivalent to solid solutions of spinel lithium ferrite with Fe_3O_4 on rapid cooling and to solid solution of lithium ferrite and $\gamma\text{-Fe}_2\text{O}_3$ with precipitation of $\alpha\text{-Fe}_2\text{O}_3$ on slow cooling. Lithium losses and $\alpha\text{-Fe}_2\text{O}_3$ precipitate amounts are calculated. The magnetic moment and lattice parameter of stoichiometric lithium ferrite have been determined: magnetic moment at 25°C : $3736 \pm 20\text{G}$; lattice parameter at 28°C : $8.3293 \pm 0.0005\text{\AA}$.

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