

Neutron Diffraction and Mössbauer Study of Ordered and Disordered  $\text{LiFeO}_2$ †

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Neutron diffraction and Mössbauer studies of two crystallographic forms of  $\text{LiFeO}_2$  have been made. The ordered tetragonal form, in which there is cation order similar to that in  $\text{CuFeS}_2$ , becomes antiferromagnetic below 315°K. Good neutron intensity agreement is obtained with a collinear spin structure in which there is strong antiferromagnetic superexchange between  $\text{Fe}^{3+}$  ions in (001) planes, but only weak coupling between the planes. The moments are directed along the [001] axis and the magnetic symmetry is tetragonal. Identical calculated intensities are given by a second collinear structure of lower symmetry in which ferromagnetic (111) planes of moments are coupled antiparallel, but the x-ray data are not consistent with this model. However, this type of structure is realized in disordered, cubic  $\text{LiFeO}_2$  below 90°K, although both the neutron scattering and the Mössbauer spectra reveal that the long-range magnetic order is far from complete.

## 1. INTRODUCTION

NEUTRON diffraction studies of the magnetic structures of mixed metal oxide systems have been confined mainly to compounds having crystal structures of spinel, hematite-ilmenite, or perovskite type. No attempts appear to have been made to extend such studies to the rather large group of mixed oxides having the general formula  $A^{1+}B^{3+}O_2$  in which  $A$  is commonly Li, Na, K, Ag, or Cu, and  $B$  any one of the trivalent  $3d$ , or sometimes  $4d$ , cations. A majority of these compounds possess structures closely related to the rocksalt type of lattice found in the  $3d$  transition metal monoxides. The latter were, of course, among the first magnetic compounds to be studied by neutron diffraction techniques,<sup>1</sup> and the elucidation of their magnetic structures provided important experimental support for the basic concept of superexchange advanced by Anderson.<sup>2</sup> By taking advantage of the various cation ordering schemes found in the related mixed oxides, it is hoped that neutron diffraction and magnetic studies of some of these compounds which are in progress will throw more light on the nature of particular interactions. Some results for  $\text{LiFeO}_2$  are presented in this paper.

$\text{LiFeO}_2$  appears to be a particularly advantageous choice as it allows the use of the Mössbauer technique<sup>3,4</sup> as an additional experimental tool applicable to the study of magnetism. This material is also known to have three structural modifications. There is a disordered form which was found by Posnjak and Barth<sup>5</sup> to have the rocksalt type of lattice [Fig. 1(a)], and which was one of the earliest examples of a compound in which two cations were observed to be distributed at random on a single set of lattice sites. These authors also noted the

existence of an anisotropic modification, whose structure was later established by Barblan, Brandenberger, and Niggli.<sup>6</sup> In this form the cations are ordered as in Fig. 1(b) and the unit cell is tetragonal, consisting of two basic units of rocksalt type. A third low-temperature form, also tetragonal, has been obtained by Collongues<sup>7</sup> and consists of a single basic layer of rocksalt type in which there are alternating layers of Li and Fe ions [Fig. 1(c)].

It is helpful at this stage to outline some of the features of the magnetic structures of the transition metal monoxides, in which magnetic order of the second kind is found below the respective Néel temperatures.<sup>1,8</sup> The magnetic moments within a given (111) layer are parallel, and their direction in successive layers alter-

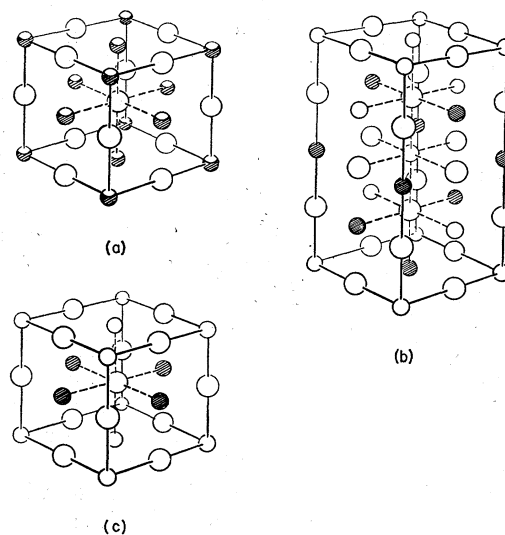


FIG. 1. The three crystal modifications of  $\text{LiFeO}_2$ . Small open circles denote  $\text{Fe}^{3+}$ , shaded circles  $\text{Li}^+$ , and large open circles  $\text{O}^{2-}$ . Partially shaded circles represent a random distribution of  $\text{Fe}^{3+}$  and  $\text{Li}^+$ .

† Part of this work was reported at the A.C.A. annual meeting, Villanova (1962).

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<sup>1</sup> C. G. Shull, W. A. Strauser, and E. O. Wollan, *Phys. Rev.* **83**, 333 (1951).

<sup>2</sup> P. W. Anderson, *Phys. Rev.* **79**, 350, 705 (1950).

<sup>3</sup> R. L. Mössbauer, *Z. Physik* **151**, 124 (1958).

<sup>4</sup> G. K. Wertheim, *J. Appl. Phys. Suppl.* **32**, 110S (1961).

<sup>5</sup> E. Posnjak and T. F. W. Barth, *Phys. Rev.* **38**, 2234 (1931).

<sup>6</sup> F. Barblan, E. Brandenberger, and P. Niggli, *Acta Helv. Chim.* **27**, 88 (1944).

<sup>7</sup> R. Collongues, *Compt. Rend.* **241**, 1577 (1955).

<sup>8</sup> W. L. Roth, *Phys. Rev.* **110**, 1333 (1958).

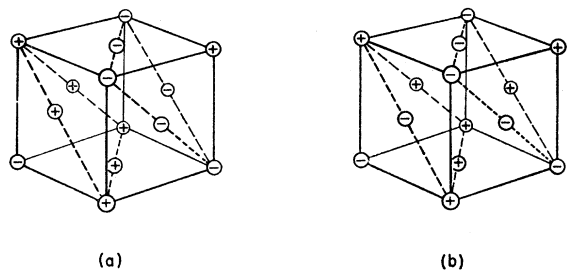


FIG. 2. One octant of the magnetic unit cells of (a) structure *A* (b) structure *B*, as described in text for oxides of MnO type. Oxygen ions have been omitted.

nates in a positive and negative sense, as illustrated in Fig. 2(a). The predominant interaction, which is negative, is between a cation and its six next-nearest neighbors via the intervening oxygen ions, the cation-anion-cation angles being  $180^\circ$ . Six of its twelve nearest-neighbor cations have parallel moments and six have antiparallel moments, the cation-anion-cation angles being about  $90^\circ$  in this case. The configurational magnetic symmetry,<sup>9</sup> which is defined by considering the moments as positive and negative (or black and white) entities, and which neglects their vector nature, is clearly rhombohedral, and the number of magnetically equivalent (111) planes is, of course, only two. A second collinear structure, with precisely the same over-all numbers of parallel and antiparallel nearest- and next-nearest-neighbor moments with respect to that on a given cation, was recognized by Li<sup>10</sup> [Fig. 2(b)], who designated this structure *B* and the other *A*. The configurational symmetry of this is cubic, and although the squares of the magnetic structure factors have values only one quarter of those appropriate to the first model, the number of magnetically equivalent (111) planes for example, is eight. It is easy to show that an analogous relationship is valid for the other reflections, and thus the values of  $j|F_{hkl}|^2$  are identical for the two structures. In general, this ambiguity can be resolved when the direction of the moments is taken into account for  $\langle q^2 \rangle$  assumes different values in each case. In this way Roth<sup>8</sup> was able to assign structure *A* to the transition metal monoxides from powder neutron data alone.

However, in the event that the moments are directed along one of the cube axes, powder data cannot distinguish between the two structures, as the respective values of  $\langle q^2 \rangle$  are then identical as well. It has also been shown that a number of multispin axis models may be devised which give equally good agreement with the powder neutron data.<sup>11,12</sup> In the case of NiO, structure *A* has been uniquely confirmed by studies of an almost single domain, single crystal,<sup>13,14</sup> but in the case of MnO,

FeO, and CoO, the absence of such data leaves some ambiguity. However, it is known that crystallographic distortions occur at the Néel temperatures of these compounds which lower the symmetry to rhombohedral,<sup>15,16</sup> except in the case of CoO, which becomes tetragonal.<sup>17</sup> A theoretical evaluation of the various forms of anisotropy energy by Kanamori,<sup>18</sup> based upon structure *A*, predicts distortions which are generally quite close in nature and magnitude to those actually observed. It is therefore reasonable to assume that this structure is correct.

The subsequent description will show that an analogous situation applies to the ordered form of LiFeO<sub>2</sub>, but that in this case the experimental evidence tends to favor a structure of *B* type.

## 2. PREPARATION OF SAMPLES

The phase relationships among the three modifications of LiFeO<sub>2</sub> have been examined in some detail by Fayard,<sup>19</sup> and are quite complicated. The stable ordered form, designated *Q<sub>I</sub>* [Fig. 1(b)], transforms to the stable disordered form *C* [Fig. 1(a)] at about 670°C. Below this temperature *C* is metastable, and after an involved cyclic heat treatment, transforms to the metastable ordered form *Q<sub>II</sub>* [Fig. 1(c)] at about 580°C. The latter in turn undergoes a continuous transformation to *Q<sub>I</sub>* at temperatures below 580°C. Between 580°C and 670°C, *Q<sub>I</sub>* and *C* are supposed to be able to coexist.

The cubic form *C* was obtained by heating a mixture of reagent grade Li<sub>2</sub>CO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> at 900°C, and reheating at the same temperature a compacted disk of the well-ground product, which was then quenched in CCl<sub>4</sub>. The x-ray powder pattern, taken with Fe *K* $\alpha$  radiation, revealed a single face-centered cubic phase with very sharply resolved doublets. The lattice parameter was 4.157 Å, in good agreement with previous published figures, although Fayard<sup>19</sup> stresses the variability of the parameter according to departures from stoichiometry and the quenching temperature. The latter effect he attributes to the development of short-range cation order at lower temperatures. Chemical analysis for Fe gave a value of 58.7% (theoretical is 58.9%).

The preparation of the stable ordered form *Q<sub>I</sub>* was accomplished in a similar way at about 625°C. The powder pattern showed the expected tetragonal phase, with quite well-resolved doublets, but also revealed the presence of a small quantity of the cubic material. The lattice parameters of the tetragonal phase were  $a=4.048$  Å and  $c=8.737$  Å, also in good agreement with previous results.<sup>6,19</sup> Chemical analysis for Fe gave a value of 58.2%.

Attempts to prepare the metastable ordered form *Q<sub>II</sub>* from Li<sub>2</sub>CO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> following the heat treatment

<sup>9</sup> G. Shirane, *Acta Cryst.* **12**, 282 (1959).

<sup>10</sup> Y. Y. Li, *Phys. Rev.* **110**, 627 (1955).

<sup>11</sup> W. L. Roth, *Phys. Rev.* **111**, 772 (1958).

<sup>12</sup> F. Keffer and W. O'Sullivan, *Phys. Rev.* **108**, 637 (1957).

<sup>13</sup> W. L. Roth and G. A. Slack, *J. Appl. Phys. Suppl.* **31**, 352S (1960).

<sup>14</sup> H. A. Alperin, *J. Appl. Phys. Suppl.* **31**, 354S (1960).

<sup>15</sup> H. P. Rooksby, *Acta Cryst.* **1**, 226 (1948).

<sup>16</sup> B. T. M. Willis and H. P. Rooksby, *Acta Cryst.* **6**, 827 (1953).

<sup>17</sup> N. C. Tombs and H. P. Rooksby, *Nature* **165**, 442 (1950).

<sup>18</sup> J. Kanamori, *Progr. Theoret. Phys. (Kyoto)* **17**, 197 (1957).

<sup>19</sup> M. Fayard, *Ann. Chim. (Paris)* **6**, 1279 (1961).

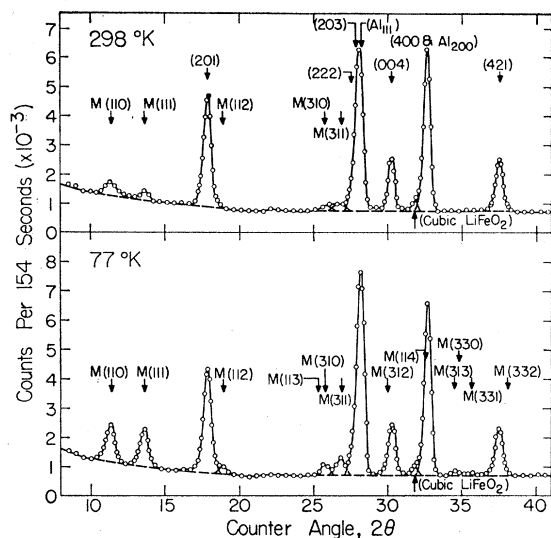


FIG. 3. Neutron diffraction patterns from tetragonal  $\text{LiFeO}_2$  at 298 and 77°K. Indices based on cell with  $a=8.096 \text{ \AA}$ ,  $c=8.737 \text{ \AA}$ . Magnetic reflections prefixed by  $M$ .

outlined by Fayard<sup>19</sup> have so far been unsuccessful, possibly because a more chemically reactive form of  $\text{Fe}_2\text{O}_3$  is required, such as that used by Fayard. Work is in progress in an attempt to obtain and study this particular form of  $\text{LiFeO}_2$ .

### 3. TETRAGONAL $\text{LiFeO}_2$

#### Neutron Diffraction Data

These were obtained at the Westinghouse testing reactor from a powder sample contained in a thin-walled aluminum tube about  $\frac{3}{8}$  in. in diameter and 2 in. in length. The neutron wavelength was 1.140  $\text{\AA}$ . The diffraction pattern at 298°K is shown in the upper half of Fig. 3. With the exception of a few small peaks of magnetic origin and one from cubic  $\text{LiFeO}_2$ , the pattern can be indexed in agreement with the space group  $I4_1/amd(D_{4h}^{19})$  assigned by Barblan *et al.*<sup>6</sup> In order to later index the magnetic peaks, all the indices in Fig. 3 are based upon a doubled cell with  $a=8.096 \text{ \AA}$  and  $c=8.737 \text{ \AA}$ . The atoms are in the following special positions<sup>20</sup>: Fe in (4a), Li in (4b), and O in (8e). The oxygen positions involve one variable parameter  $z$ . Agreement between calculated and observed nuclear intensities is very satisfactory if this parameter is given the value  $0.232 \pm 0.002$  (Table I). The apparent discrepancy in the case of the (004) reflection is caused by a small magnetic contribution to the observed intensity. No noticeable improvement can be obtained by assuming a slight degree of either additional order of  $Q_{11}$  type or disorder of  $C$  type. The amount of the cubic phase present estimated from its (200) reflection is about 6%. The value found for  $z$  corresponds to a dis-

<sup>20</sup> *International Tables for X-Ray Crystallography* (The Kynoch Press, London, England, 1952), Vol. 1.

placement of two of the oxygen ions towards the more highly charged  $\text{Fe}^{3+}$  ions, such that all six Fe-O distances become about 2.03  $\text{\AA}$  and the oxygen octahedra are therefore fairly regular. Four of the six Li-O distances are also 2.03  $\text{\AA}$ , but the remaining two are much larger, about 2.34  $\text{\AA}$ . A rather similar situation exists in the isomorphous compound<sup>21</sup>  $\text{LiScO}_3$  for which  $z=0.23$ .

The diffraction pattern at 77°K shown in the lower half of Fig. 3 reveals an enhancement of the intensities of a number of peaks. These may be indexed on the basis of the doubled cell mentioned above, and only reflections with both  $h$  and  $k$  odd are observed, which immediately suggests that the Fe ions in basal planes are coupled antiferromagnetically as would be expected for superexchange through this almost 180° cation-oxygen-cation configuration [see Fig. 1(b)]. Coupled with the fact that an x-ray pattern taken at 77°K reveals the unit cell still to be tetragonal ( $a=4.042 \text{ \AA}$ ,  $c=8.716 \text{ \AA}$ ), the use of magnetic space groups<sup>22</sup> shows that the most symmetrical structure consistent with the observed intensities belongs to the space group  $Pc4_3$ -No. 78-23,<sup>23</sup> with positive (or white) moments in  $x, y, z$ , etc., and negative (or black) moments in  $\frac{1}{2}+x, \frac{1}{2}+y, z$ , etc., the moments being directed along the [001] axis. With the "ideal" parameters  $x=0, y=-0.25$ , and  $z=0$ , the relative positions of the Fe ions in the chemical and magnetic unit cells remain unchanged. Intensity data are summarized in Table II. The structure is illustrated in Fig. 4(a), and is closely related to the  $B$  type of structure described by Li<sup>10</sup> from which it may be derived by replacing the appropriate moments by nonmagnetic lithium ions.

In Fig. 4(b) is shown a second collinear structure which satisfies the requirements of antiferromagnetic coupling in the basal plane and which may be derived in

TABLE I. Comparison of observed and calculated nuclear relative intensities for tetragonal  $\text{LiFeO}_2$ . Scattering amplitudes of 0.96,  $-0.18$ , and  $0.58 \times 10^{-12} \text{ cm}$  have been assigned to Fe, Li, and O, respectively.<sup>a</sup> Value of oxygen parameter  $z$  taken as 0.232. Indices are based upon a cell with  $a=8.096 \text{ \AA}$  and  $c=8.737 \text{ \AA}$ .

$hkl$	Relative intensities at 298°K	
	Calculated	Observed
201	245	247
004	91	102
421	118	112
205	95	94
423	32	27
404	175	183
601	35	26
226	1	<4
425	122	123

<sup>a</sup> C. G. Shull and E. O. Wollan, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2, p. 137.

<sup>21</sup> C. J. M. Rooymans, *Z. Anorg. Allgem. Chem.* **313**, 234 (1961).  
<sup>22</sup> G. Donnay, L. M. Corliss, J. D. H. Donnay, N. Elliott, and J. M. Hastings, *Phys. Rev.* **112**, 1917 (1958).

<sup>23</sup> N. V. Belov, N. N. Neronova, and T. S. Smirnova, *Kristallografiya* **2**, 315 (1957) [translation: *Soviet Phys.—Cryst.* **2**, 311 (1957)].

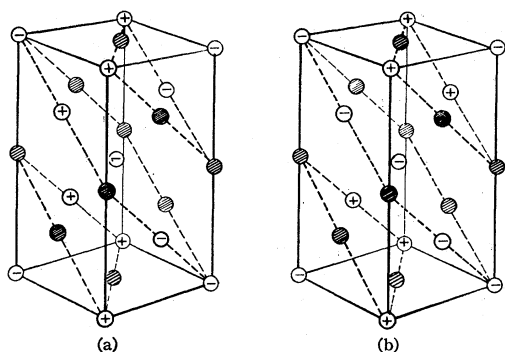


FIG. 4. One quarter of the magnetic unit cells of (a) structure *B* (b) structure *A*, as described in text for tetragonal  $\text{LiFeO}_2$ . Shaded circles denote  $\text{Li}^+$ . Oxygen ions have been omitted.

a similar way from the *A* type of structure found in the transition metal monoxides. With the moments directed along  $[001]$ , the ambiguity described earlier arises and it is impossible to discriminate between the two structures from powder neutron data alone as the calculated intensities are identical. However, it can readily be seen from a model that the fourfold axis is destroyed. Since this lower symmetry is not revealed in the x-ray pattern, model *B* is to be preferred, although it must be noted that the absence of a detectable distortion may not be altogether conclusive evidence for rejecting structure *A* or any multispin axis models which give satisfactory intensity agreement.

In both *A* and *B*, an Fe ion has four next-nearest Fe neighbors with antiparallel moments, consistent with strong antiferromagnetic coupling in the (001) planes, and four nearest Fe neighbors, two with parallel and two with antiparallel moments, a situation analogous to that in FeO. There is an important difference, however. To create long-range order along  $[001]$  relatively weak

TABLE II. Comparison of observed and calculated magnetic relative intensities for tetragonal  $\text{LiFeO}_2$ . Form factor for  $\text{Fe}^{3+}$  as given by Nathans *et al.*<sup>a</sup> Indices are based upon a cell with  $a=8.096 \text{ \AA}$  and  $c=8.737 \text{ \AA}$ .

<i>hkl</i>	Relative intensities at 77°K		Relative intensities at 298°K	
	Calculated <sup>b</sup>	Observed	Calculated <sup>c</sup>	Observed
110	102	97	36	43
111	92	93	33	14
112	21	16	7	5
113	5	26	2	14
310	21		7	
311	33	44	12	21
312	18	22 <sup>d</sup>	6	11 <sup>d</sup>
114	1	obscured	0	obscured
313	8	10	3	<4
330	3		1	
331	5	6	2	<4
332	4	obscured	1	obscured
115	0		0	
314	3	<4	1	<4

<sup>a</sup> R. Nathans, S. J. Pickart, and H. A. Alperin, *J. Phys. Soc. Japan* 17, Suppl. BIII, 7 (1962).

<sup>b</sup> Calculated with a moment of  $4.5 \mu_B$  per Fe ion.

<sup>c</sup> Calculated with a moment of  $2.7 \mu_B$  per Fe ion.

<sup>d</sup> Difference of calculated and observed nuclear intensities for 004.

TABLE III. Values of the hyperfine field  $H_i$ , isomer shift  $\Delta E$ , and quadrupole splitting  $\epsilon$ , for cubic and tetragonal  $\text{LiFeO}_2$ . The sign of  $\epsilon$  for cubic  $\text{LiFeO}_2$  is undetermined (see text). Data for  $\alpha \text{Fe}_2\text{O}_3$  are given for comparison.

	$\Delta E (\pm 0.03)$ mm/sec at 300°K	$\epsilon (\pm 0.03)$ mm/sec at 300°K	$H_i (\pm 5 \text{ kOe})$
Tetragonal $\text{LiFeO}_2$	0.53	-0.13	515 (77°K)
Cubic $\text{LiFeO}_2$	0.50	$\pm 0.28$	495 (4°K)
$\alpha \text{Fe}_2\text{O}_3$	0.51	+0.20	517 (300°K)

interactions between nearest neighbors, or via two or more oxygen ions, are an essential part of the ordering scheme.

The scale factor employed in Table II corresponds to a moment of  $4.5 \pm 0.2 \mu_B$  per Fe ion, quite close to the theoretical value of about  $4.9 \mu_B$  at 77°K. At room temperature, intensity agreement is decidedly poor, even allowing for experimental uncertainties, and a deviation of the spin axis from  $[001]$  may occur. To obtain the figures in Table II, a moment of  $2.7 \mu_B$  per Fe ion has been assigned at 298°K, but this may clearly be in error by at least  $0.5 \mu_B$ . However, a value of  $2.7 \mu_B$  is in fair agreement with that given by the subsequent Mössbauer study, and the discrepancies do not affect the general conclusions.

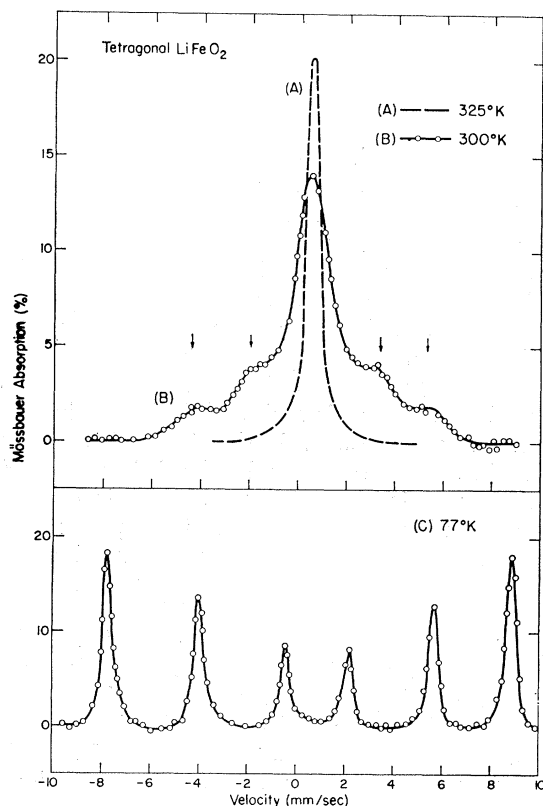


FIG. 5. Mössbauer absorption spectra from tetragonal  $\text{LiFeO}_2$  at various temperatures. Positive velocity corresponds to a movement of source towards absorber.

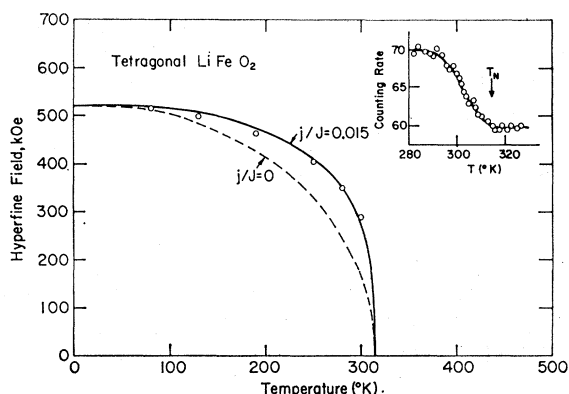


FIG. 6. Variation of hyperfine field in tetragonal  $\text{LiFeO}_2$  with temperature. The inset shows the height of the paramagnetic absorption peak as a function of temperature in the vicinity of the Néel point. The broken line represents the Brillouin function with  $S = \frac{5}{2}$ , and the solid line the function modified by the inclusion of a biquadratic exchange term.

### Mössbauer Data

These were obtained both on the apparatus previously described,<sup>24</sup> which employs a multichannel analyzer coupled with an instantaneous velocity measurement, and on a constant velocity apparatus more recently devised.<sup>25</sup>  $\text{Co}^{57}$  diffused in Cr was used as a source, giving an isomer shift  $\Delta E$  of  $+0.05$  mm/sec for a stainless steel absorber and  $+0.15$  mm/sec for one of pure iron. Samples were prepared from the materials used in the neutron diffraction study, with a thickness corresponding to  $15$  mg/cm<sup>2</sup> of natural iron.  $\alpha\text{-Fe}_2\text{O}_3$  was used as a standard, and gave the values listed in Table III for the isomer shift  $\Delta E$ , the quadrupole splitting  $\epsilon (= \frac{1}{4}e^2qQ)$ , and the hyperfine field  $H_i$  coupled with an experimental linewidth  $2\Gamma$  of  $0.40$  mm/sec.

The most interesting feature of the spectra from tetragonal  $\text{LiFeO}_2$  is the behavior near the Néel temperature, which is indicated to be slightly above room temperature by the neutron diffraction data.

At  $325^\circ\text{K}$  (Fig. 5, line A) a fairly sharp paramagnetic peak is observed. Below  $315^\circ\text{K}$ , this center peak becomes progressively broader as the temperature is lowered, and at the same time a broadened set of six peaks develops (Fig. 5, line B). Below  $290^\circ\text{K}$ , the paramagnetic peak is no longer present, and the spectra consist of a well defined set of six peaks (Fig. 5, line C). The hyperfine field is shown as a function of temperature in Fig. 6. The inset to this figure illustrates the temperature dependence of the height of the paramagnetic peak in the vicinity of the transition temperature, which is seen to be at about  $315^\circ\text{K}$ . The temperature dependence of the hyperfine field, which is assumed to be proportional to the ordered moment, differs quite considerably from that given by the appropriate Brillouin function shown by the broken line.

<sup>24</sup> S. L. Ruby and D. E. Bolef, Phys. Rev. Letters **5**, 5 (1960).

<sup>25</sup> P. A. Flinn (unpublished).

A similar tendency is observed in  $^1\text{MnO}$  and  $^{11}\text{NiO}$ , and recent interpretation of this data by Rodbell *et al.*<sup>26</sup> indicates that this arises from a small biquadratic contribution of the form<sup>27</sup>  $j(\mathbf{S}_1 \cdot \mathbf{S}_2)^2$  to the exchange energy, which is normally assumed to be of the form  $J\mathbf{S}_1 \cdot \mathbf{S}_2$  in the molecular field treatment. If  $j/J$  is given the value  $0.015$ , as for  $\text{MnO}$ , excellent agreement is obtained as shown by the solid line in Fig. 6. The steepness of the curve near  $T_N$  and the coexistence of two phases suggest that this may be a first-order transition. Possibly also the strong two-dimensional character of the interaction scheme plays some role.

An examination of the spectrum observed at  $77^\circ\text{K}$  shows that the inner four lines are shifted with respect to the outermost pair because of a small quadrupole interaction  $\epsilon (= \frac{1}{4}e^2qQ)$ . The knowledge of the spin direction, determined by neutron diffraction to be along  $[001]$ , enables  $\epsilon$  to be assigned a value of  $-0.13$  mm/sec. This value is independent of temperature in the range  $77^\circ$ – $290^\circ\text{K}$ . At higher temperatures, when the compound is paramagnetic, this quadrupole splitting is too small to be resolved, but reveals itself as a line-broadening effect, such that  $2\Gamma$  is  $0.7$  mm/sec compared with  $0.5$  mm/sec in the antiferromagnetic state. This difference is quite consistent with the above value of  $\epsilon$  in the latter state.

Magnetic susceptibility measurements in the transition region and down to  $77^\circ\text{K}$  did not reveal any antiferromagnetic peak. Unfortunately, a small spontaneous moment complicated the interpretation, and it is uncertain if the susceptibilities obtained by the usual extrapolation process reflect the true behavior of the compound. A moment of this sort could arise from

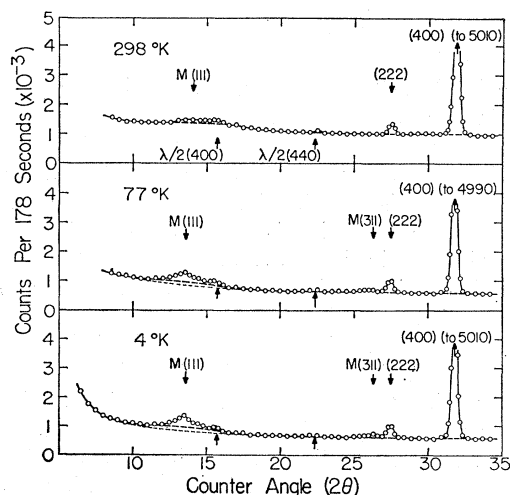


FIG. 7. Neutron diffraction patterns from cubic  $\text{LiFeO}_2$  at various temperatures. Indices based on cell with  $a = 8.314$  Å.

<sup>26</sup> D. S. Rodbell, I. S. Jacobs, J. Owen, and E. A. Harris, Phys. Rev. Letters **11**, 10 (1963).

<sup>27</sup> This  $j$  should not be confused with that used earlier to denote the multiplicity factor.

TABLE IV. Comparison of observed and calculated nuclear relative intensities for cubic  $\text{LiFeO}_2$  at  $298^\circ\text{K}$ . Scattering amplitudes as in Table I. The calculated intensities include a temperature factor  $B$  of  $0.3 \times 10^{-16} \text{ cm}^2$ . Indices are based upon a cell with  $a = 8.314 \text{ \AA}$ .

$hkl$	Relative intensities	
	Calculated	Observed
222	15	21
400	226	224
440	227	224
622	13	15
444	102	101

impurities such as ferrimagnetic  $\text{LiFe}_5\text{O}_8$ , or from a slight degree of some additional ordering process. Attempts were made to prepare samples having no spontaneous moment, but in vain.

#### 4. CUBIC $\text{LiFeO}_2$

##### Neutron Diffraction Data

These were obtained as before except that the sample was contained in a thin-walled vanadium tube. Diffraction patterns at  $298^\circ\text{K}$ ,  $77^\circ\text{K}$ , and  $4^\circ\text{K}$  are shown in Fig. 7, and agreement between calculated and observed nuclear intensities at  $298^\circ\text{K}$  is very satisfactory (Table IV). The indices are based upon a cell with a doubled edge of  $8.314 \text{ \AA}$ , and some diffuse scattering in the vicinity of the (111) position is also apparent.

The Mössbauer data described later show that a magnetic transition occurs at  $90^\circ\text{K}$ , and in support of this, some enhancement of intensity in the (111) and (311) positions can be seen at  $77^\circ$  and  $4^\circ\text{K}$ , this being a characteristic feature of magnetic ordering of the second kind. If the room-temperature data are subtracted from those at  $4^\circ\text{K}$ , as shown very roughly by the thicker broken line in Fig. 7, a small fairly coherent peak in the (111) position remains, with an intensity corresponding to an ordered moment of some  $2.5 \mu_B$  per Fe ion on the assumption that the structure is of  $\text{MnO}$  type with the spin axis lying in the (111) plane. The intensity of (311) is consistent with this assumption. If the whole of the diffuse scattering is included, according to the thinner broken line in Fig. 7, a value of about  $4.5 \mu_B$  per Fe ion is obtained. The corresponding values at  $77^\circ\text{K}$  are only slightly smaller.

The diffuse scattering at  $298^\circ\text{K}$  was initially thought to be magnetic in origin, but in view of the relatively low transition temperature, the alternative possibility of some short-range cation order was considered. Measurement of the x-ray diffuse scattering at  $298^\circ\text{K}$  showed that this was indeed the case. A very interesting feature of the pattern was that the diffuse scattering was more pronounced in the vicinity of the (111) position than in that of the (200) and (201) positions, consistent with the neutron data. If the short-range order were of the type associated with either of the tetragonal forms, diffuse scattering should occur primarily around the

latter positions, and it therefore appears that there is also a strong tendency for the Fe and Li ions to order on alternate (111) planes. Although such a modification has not been reported for  $\text{LiFeO}_2$ , related compounds such as<sup>28</sup>  $\text{NaFeO}_2$  and<sup>29</sup>  $\text{LiCrO}_2$  are known to have this type of rhombohedral structure.

##### Mössbauer Data

The spectra from cubic  $\text{LiFeO}_2$  reveal quite clearly that there is a magnetic transition around  $90^\circ\text{K}$ . At this point, the sharp doublet shown in Fig. 8(a) starts to diminish in height, and at  $77^\circ\text{K}$  and down to  $55^\circ\text{K}$ , only a very broad central hump remains. This, coupled with the neutron data, shows that the magnetic order is far from being typically long-range in nature. At  $4^\circ\text{K}$ , though, a well-defined set of six peaks is observed [Fig. 8(b)], probably as a result of an increase in domain size.

The well-resolved doublet in the paramagnetic phase is an unexpected result. It appears that this doublet must be interpreted as a quadrupole splitting, thus

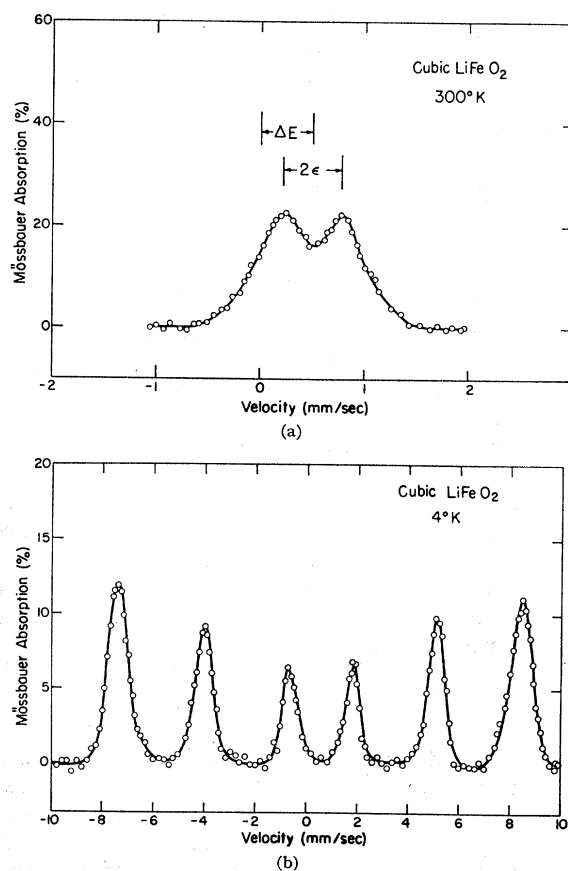


Fig. 8. Mössbauer absorption spectrum from cubic  $\text{LiFeO}_2$  at (a)  $300^\circ\text{K}$ , (b)  $4^\circ\text{K}$ .  $\Delta E$  is the isomer shift and  $\epsilon$  is the quadrupole splitting.

<sup>28</sup> S. Goldshtaub, Bull. Soc. Franc. Minéral. **58**, 6 (1935).

<sup>29</sup> W. Rüdorff and H. Becker, Z. Naturforsch. **9B**, 614 (1954).

giving  $2\epsilon = 0.56 \pm 0.05$  mm/sec. This value remains constant between  $90^\circ$  and  $520^\circ\text{K}$ . Another important characteristic of the doublet is the sharpness of the individual components, which have estimated linewidths of 0.50 mm/sec, only slightly greater than the expected single linewidth of 0.40 mm/sec. A similar quadrupole splitting in a pseudocubic environment has previously been observed for  $\text{Fe}^{2+}$  in the Mössbauer spectra of the  $\text{FeO-MgO}$  system.<sup>30</sup> However, the  $S$  state of the  $\text{Fe}^{3+}$  ion makes the present effect in  $\text{LiFeO}_2$ , particularly the well-defined value of  $\epsilon$ , rather difficult to understand. The origin of the effect very probably lies in the drastically asymmetric charge distribution associated with the random distribution of  $\text{Li}^{1+}$  and  $\text{Fe}^{3+}$  ions on neighboring equivalent sites, but  $\epsilon$  might then be expected to have different values according to the particular numbers and distribution of these ions surrounding a given Fe ion.

This quadrupole effect did not reveal itself, as expected, by a shift in the line positions in the magnetically ordered state at  $4^\circ\text{K}$ , but instead gave rise to line broadening. This is understandable if the electric field gradient axis can have any one of several directions because of local inhomogeneities, but the spin axis is fixed along some unique magnetically determined direction. Susceptibility measurements were once again hampered by a small spontaneous moment ( $\sim 0.1$  emu/g), but it appeared that a Curie-Weiss law was obeyed above room temperature, with an asymptotic Néel temperature of  $-450 \pm 50^\circ\text{K}$  and an effective moment of  $5.6 \pm 0.4 \mu_B$ . However, no susceptibility peak was observed on passing through  $90^\circ\text{K}$  down to  $50^\circ\text{K}$ . A similar effect has been noticed in the  $\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$

system,<sup>31</sup> in which there is also a considerable "deficit" in the ordered moments, and probably reflects the incompleteness of the long-range magnetic order in these solid solutions.

## 5. SUMMARY AND CONCLUSIONS

The preceding structure determinations show that the essential features of the magnetic structures of the transition metal monoxides are preserved in the related modifications of  $\text{LiFeO}_2$ , the principal exchange interaction being a negative one between next-nearest Fe neighbors. One interesting difference arises if, as is probable, the tetragonal form has the  $B$  type of structure.

Although both the Mössbauer and neutron data show that a definite antiferromagnetic transition occurs in both materials, it is likely that short-range cation order in cubic  $\text{LiFeO}_2$  and the two-dimensional nature of the interaction scheme in tetragonal  $\text{LiFeO}_2$  play an important role in determining the exact nature of the transition regions. The Mössbauer study is particularly valuable in cases such as these where interpretation of susceptibility measurements is hampered by some impurity effect.

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<sup>30</sup> G. Shirane, D. E. Cox, and S. L. Ruby, Phys. Rev. **125**, 1158 (1962).

<sup>31</sup> D. E. Cox, G. Shirane, and W. J. Takei, J. Phys. Chem. Solids **24**, 405 (1963).