

Neutron Diffraction Studies of Magnesium Ferrite-Aluminate Powders

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(Received 9 August 1952)

Neutron diffraction measurements with magnesium ferrite aluminates support the suggestion of Jones & Roberts that all the Al^{3+} ions in these compounds go into B sites. The neutron data are able to distinguish between the Mg^{2+} and Al^{3+} ions, and are sensitive to the value of the oxygen parameter u . The values of u deduced for MgFe_2O_4 and MgFeAlO_4 are 0.382 ± 0.002 and 0.385 ± 0.002 respectively.

Introduction

Measurements of the saturation magnetization at low temperatures of magnesium ferrite, MgFe_2O_4 , and solid solutions of this compound with MgAl_2O_4 have been reported by Jones & Roberts (1952). It is concluded, in agreement with a suggestion by Gorter (1950), that these compounds have an incompletely inverted spinel structure with about 20% greater occupation of B sites than of A sites by the Fe^{3+} ions. Thus in the case of MgFe_2O_4 the tetrahedrally co-ordinated A sites are occupied by $\text{Mg}_{0.1}\text{Fe}_{0.9}$ and the octahedral B sites by $\text{Mg}_{0.9}\text{Fe}_{1.1}$, in contrast with Fe , MgFe which would be expected in A , B respectively for a fully inverted spinel structure and with Mg , 2 Fe which would be found in A , B for a 'normal' structure. Jones & Roberts suggest that in the mixed ferrites all the Al^{3+} ions go into B sites, causing progressive reversion of the Mg^{2+} into A sites and achieving a regular transformation from the largely 'inverse' MgFe_2O_4 structure to the 'normal' arrangement in MgAl_2O_4 .

The present paper provides evidence in support of these conclusions from the neutron diffraction patterns of these materials.

Advantage of neutron diffraction

The use of neutron diffraction offers a number of advantages over X-ray techniques in investigating the structural arrangements of these compounds.

First, the scattering amplitudes of aluminium and magnesium for neutrons are significantly different, being 0.35 and 0.52×10^{-12} cm. respectively, in contrast to their near identity for X-rays. The latter figure is a recently redetermined value (Bacon, 1952). It is found possible by careful intensity measurements to distinguish between the magnesium and aluminium positions, thus carrying the investigation of the cationic positions a good deal further than has been possible with X-rays.

Secondly, the neutron intensities are more sensitive

to the oxygen parameter u on account of the fact that the scattering amplitude of oxygen for neutrons, 0.575×10^{-12} cm., is greater than that of magnesium and aluminium and is 60% of the value for iron. On the other hand, for X-rays the oxygen scattering amplitude is appreciably less than for Mg , Al at the relevant values of $(\sin \theta)/\lambda$ and is only about 25% of that of iron. It is found that the ratio of the intensities of the neighbouring lines (511, 333) and (440+531) affords an accurate method of determining u from the experimental data.

Thirdly, additional information is obtainable from the coherent magnetic scattering which contributes to the diffraction pattern at temperatures below the Curie point.

Finally, the ease with which the neutron intensity measurements can be made on an absolute basis, aided by the direct determination of the absorption correction which is possible, greatly strengthens the conclusions which can be drawn by comparison of experimental and calculated intensities.

Experimental measurements

The measurements were made with the neutron spectrometer described by Bacon, Smith & Whitehead (1950) using cylindrical powder samples, enclosed in thin-walled (0.25 mm.) aluminium containers, which were bathed in the neutron beam. The samples were about 1.5 cm. in diameter and 3.5 cm. in length, containing about 7 cm.³ of well packed powder.

With MgFe_2O_4 , which has a Curie point of about 300° C., measurements were made at room temperature and also, by enclosing the sample in a simple wire-wound furnace, at 400° C. With MgFeAlO_4 , which has a Curie point of -30° C., readings were obtained at room temperature and at -150° C., using an aluminium Dewar vessel containing liquid air, of a design similar to that employed by Shull (1951).

The materials used were those prepared by Nicks

(1951) and used for the magnetic measurements of Jones & Roberts (1952). They had been slowly cooled from 1500° C. over a period of 12–16 hr. in an atmosphere of oxygen during preparation.

The neutron diffraction patterns were recorded automatically by connecting the output of the BF₃ detecting counter via a ratemeter to a pen recorder. The spectrometer arm was rotated, or oscillated over a portion of the diffraction pattern, with an angular velocity of 0.1° per minute. The intensities of the stronger lines were measured as the mean of the areas under the diffraction curves on four records. The low-angle portion of the pattern for MgFeAlO₄ (Fig. 1)

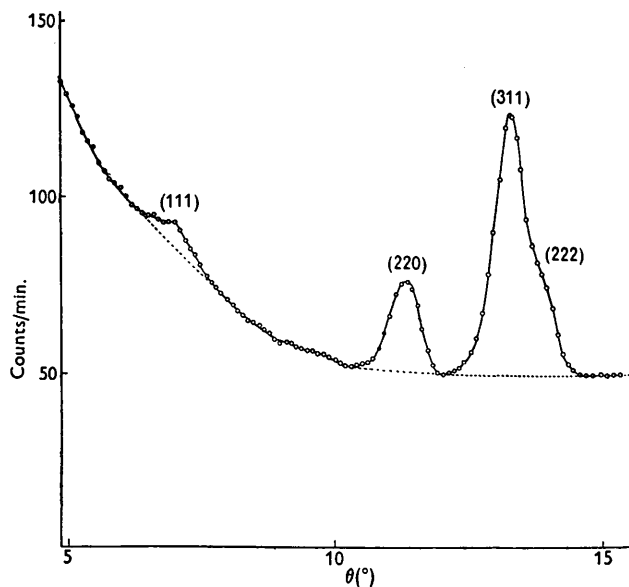


Fig. 1. Low-angle portion of neutron diffraction pattern for MgFeAlO₄.

is of particular significance in determining the structure of this compound. In order to increase the accuracy of measurement of the (111) reflexion the ordinates were summed on 23 individual records of this region, and Fig. 1 shows the mean curve obtained.

The intensities were placed on an absolute basis by comparison with those measured for a diamond sample under identical conditions, following the procedure described by Shull & Wollan (1951), assuming a coherent scattering amplitude of 0.65×10^{-12} cm. for carbon.

Discussion of results

(i) MgFe₂O₄

Fig. 2 shows the calculated variation of intensity with oxygen parameter u for the main reflexions of MgFe₂O₄ at 400° C. Curves are drawn for the 'normal' and 'inverse' structures and also for the incompletely inverted structure, favoured by the magnetic results, in which the A , B sites are occupied by Mg_{0.1}Fe_{0.9}

and Mg_{0.9}Fe_{1.1} respectively. The rapid variation with u of the intensities of the (511, 333) line and the unresolved pair (440+531) is very evident, and the

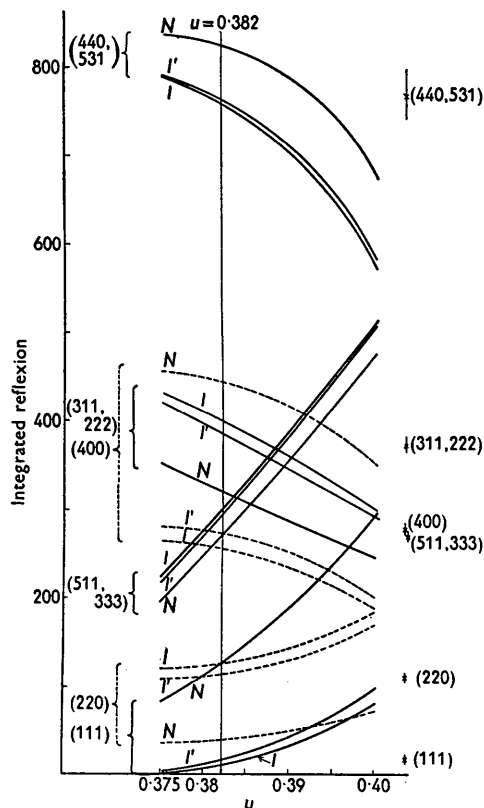


Fig. 2. MgFe₂O₄: calculated variation of nuclear reflexion intensities as a function of oxygen parameter u for the various structures defined in Table I. N is the 'normal' structure, I is 'inverse' and I' is incompletely inverted. At the right-hand side of the figure are shown the experimental intensities with the estimated errors.

ratio of these two intensities serves as a sensitive way of determining u , particularly as the lines are adjacent and will therefore have very similar corrections for thermal vibrations. By comparison with the experimental ratio of these intensities it is estimated that u for MgFe₂O₄ is equal to 0.382 ± 0.002 . This is to be compared with the value of 0.390 ± 0.006 given by Barth & Posnjak (1932) from X-ray measurements.

The calculated intensities shown in Fig. 2 are arrived at by considering nuclear reflexions only, no coherent magnetic scattering being expected at 400° C. These intensities have been corrected for absorption, using the experimentally determined value of μR , where μ is the linear absorption coefficient and R is the specimen radius, but not for thermal vibrations. The intensities obtained experimentally are shown at the right-hand side of Fig. 2 after applying a small correction for thermal vibrations, determined empirically by comparing the intensities of the higher-angle lines at 400° C. and 20° C., these lines having a negligible magnetic contribution even below the Curie

Table 1. Comparison of experimental and calculated intensities of MgFe_2O_4 : 400° C.

	Calculated intensity			Experimental intensity
	Normal structure <i>N</i> $u = 0.385$	Inverse structure <i>I</i> $u = 0.382$	Incompletely inverted <i>I'</i> $u = 0.382$	
<i>A</i> sites	Mg	Fe	$\text{Mg}_{0.1}\text{Fe}_{0.9}$	
<i>B</i> sites	Fe_2	MgFe	$\text{Mg}_{0.9}\text{Fe}_{1.1}$	
(111)	126	10	16	18 ± 3
(220)	39	127	114	112 ± 4
(311, 222)	320	400	385	374 ± 10
(400)	448	256	274	279 ± 6
(511, 333)	270	297	292	274 ± 7
(440, 531)	820	758	762	770 ± 30
Ratio (311, 222)/(400)	0.72	1.56	1.40	1.34 ± 0.06
(311, 222)/(220)	8.2	3.15	3.38	3.33 ± 0.2
(311, 222)/(111)	2.5	40	24	21 ± 4
(220)/(111)	0.31	13	7.1	6.3 ± 1.2

Table 2. Comparison of intensities of MgFe_2O_4 at 20° C. and 400° C., and of measured and calculated magnetic intensities at 20° C.

Reflexion	Experimental intensity			Calculated magnetic intensity for perfect alignment
	20° C.	400° C.	Difference 20°–400° C.	
(111)	213 ± 5	18 ± 3	195 ± 8	307
(220)	153 ± 6	112 ± 4	41 ± 10	66
(311, 222)	406 ± 6	374 ± 10	32 ± 16	29
(400)	318 ± 6	279 ± 6	39 ± 12	36
(333, 511)	259 ± 7	274 ± 7	–15 ± 14	2
(440, 531)	742 ± 10	770 ± 30	–28 ± 40	4

point. The equivalent Debye temperature is about 500° K.

Comparison of the experimental values with the calculated intensities for the three different structures shows that agreement is easily the best with the incompletely inverted structure and at $u = 0.382$. This is illustrated also in Table 1 which includes comparison of the intensity ratios of certain lines which will be practically independent of any inaccuracy in the estimated temperature correction.

At 20° C. contributions to the diffracted intensities would be expected from coherent magnetic scattering and these have been calculated for the incompletely inverted structure, in a manner similar to that described for Fe_3O_4 by Shull, Wollan & Koehler (1951), on the assumption that the magnetic moments of the Fe^{3+} ions in MgFe_2O_4 are in parallel alignment but directed in opposite senses for the *A*, *B* sites. It is not possible from examination of polycrystalline samples of this sort to determine the actual preferred direction of the electron spins relative to the crystallographic axes. For any particular reflexion plane, e.g. (111), the magnetic intensity is indeed proportional to $q^2 \equiv \sin^2 \alpha$, where α is the angle between the scattering and magnetization vectors. However, the average value of q^2 when taken over all eight faces of the {111} form reduces to $\frac{2}{3}$ whatever be the chosen direction for the magnetization, and similarly for the other reflexions. Since the magnetic structure factors for the

postulated ferromagnetic arrangement are the same for all these faces, in contrast with the case of MnO for which there is effectively a reduced multiplicity (Shull, Strauser & Wollan, 1951), it follows that the observed magnetic intensities will not be dependent on the direction of the magnetization vectors relative to the crystallographic axes.

The calculated magnetic intensities, assuming perfect alignment of the magnetic moments, are shown in the right-hand column of Table 2. The previous columns of this table show the experimental intensities at 20° C. and 400° C. respectively and their difference, which corresponds to the magnetic contribution existing at 20° C.

It is clear from the table that significant comparison of calculated and experimentally deduced magnetic intensities can be made only for the (111) and, to a less degree, the (220) reflexions. For the other reflexions any magnetic scattering effects are overwhelmed by the nuclear scattering. However, from the data given for (111), (220) it appears that at 20° C. about two-thirds of the intensity contribution for perfect alignment is obtained. From Jones & Roberts's magnetic work the ratio of the saturation magnetizations at room temperature and absolute zero is 0.83, with an estimated accuracy of about ± 0.02 . The ratio of the magnetic intensity contributions to the neutron diffraction lines should be equal to the square of this magnetization ratio, i. e. to 0.70 ± 0.03 . This is con-

Table 3. Intensity data for MgFeAlO_4 at 20°C .

u	Calculated intensity							Experimental intensity
	a	b	c	d_1	d_2 (Nicks d)	d'	d''	
A sites	0.387	0.384	0.388	0.385	0.385	0.385	0.385	
B sites	Mg	Fe	Al	$\text{Mg}_{0.5}\text{Fe}_{0.5}$	$\text{Al}_{0.5}\text{Fe}_{0.5}$	$\text{Mg}_{0.53}\text{Fe}_{0.47}$	$\text{Al}_{0.53}\text{Fe}_{0.47}$	
	AlFe	MgAl	FeMg	$\text{Mg}_{0.5}\text{AlFe}_{0.5}$	$\text{MgAl}_{0.5}\text{Fe}_{0.5}$	$\text{Mg}_{0.47}\text{AlFe}_{0.53}$	$\text{MgAl}_{0.47}\text{Fe}_{0.53}$	
(111)	69	3	141	13	26	15	29	17 ± 3
(220)	47	142	24	87	68	85	65	78 ± 4
(311, 222)	232	349	196	284	270	282	266	293 ± 5
(400)	318	164	390	236	271	240	279	246 ± 5
Ratio 311, 222/220				3.3	4.0	3.3	4.1	3.7 ± 0.2
Ratio 311, 222/111				22	10.4	19	9.2	16 ± 3
Ratio 311, 222/400				1.20	1.00	1.18	0.95	1.21 ± 0.05
Ratio 220/111				6.7	2.6	5.7	2.2	4.4 ± 0.8

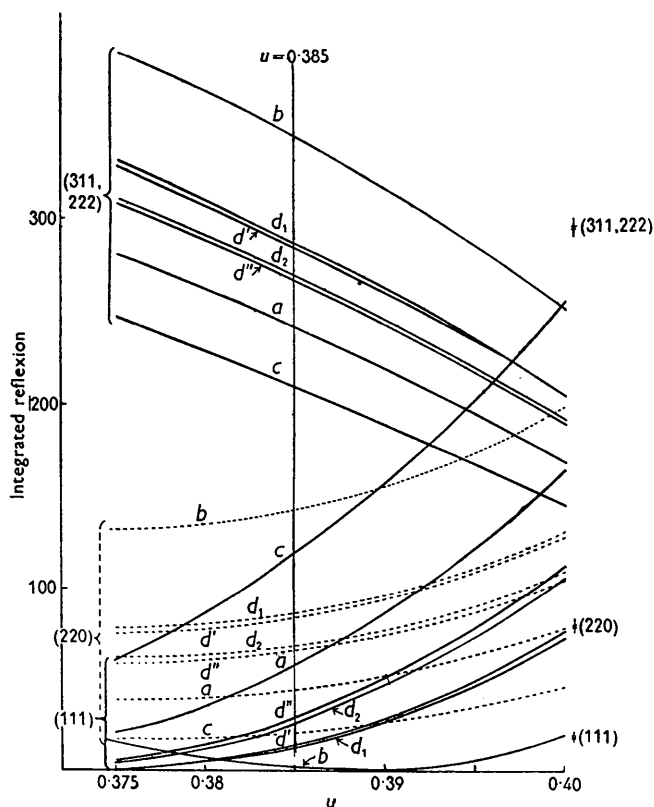


Fig. 3. MgFeAlO_4 : calculated variation of nuclear reflexion intensities with oxygen parameter u for the various structures $a, b, c, d_1, d_2, d', d''$ defined in Table 3. The experimental intensities are indicated at the right-hand side of the figure, together with the estimated errors.

sistent with the values deduced from the experimental results shown in Table 2, which give 0.64 ± 0.03 and 0.62 ± 0.15 for the (111), (220) lines respectively.

It is pointed out here that although the above calculation of magnetic scattering has been made for the incompletely inverted structure, it is not sensitive to small structural variations. The magnetic intensity of the (111) line is proportional to the factor $(4D_A - 4\sqrt{2} \cdot D_B)^2$, where D_A, D_B are the mean scattering amplitudes for an ion on A, B sites respectively. Since D_A, D_B are of opposite sign the

intensity is largely determined by the numerical sum of the magnetic moments and is only about 5% different for the purely inverse structure. On the other hand the magnetic saturation is of course proportional to the vector sum of the moments. In principle a sensitive distinction between the different models on the basis of magnetic reflexions would be provided by (311) whose intensity is proportional to $(4D_A + 4\sqrt{2} \cdot D_B)^2$, which, since D_A, D_B are of opposite sign, would be very sensitive to transfer of Fe^{3+} ions from A to B sites. However, the experimental error in

measuring the intensity of this line, which is not only predominantly nuclear but also unresolved from (222), destroys this possibility.

(ii) MgFeAlO_4

Since the Curie point of this compound is about -30°C . conclusions based on consideration of nuclear scattering alone can be drawn from the room temperature pattern, with the possibility of extracting further information from the coherent magnetic scattering which is additional to the diffraction pattern at -150°C .

The low-angle portion of the 20°C . pattern has already been referred to at Fig. 1. Calculation has been made for the various cationic distributions discussed by Nicks (1951), together with certain others which are indistinguishable by X-rays but which would show different magnetic properties. These structures are listed in Table 3, which summarizes the neutron intensity data to which attention will be drawn shortly. For each of these structures, curves of intensity versus parameter u were plotted for the various reflexions, and the experimental intensities were viewed against these curves which are shown for the lower-angle reflexions in Fig. 3. Fig. 4 shows the particular sensitivity of the ratio (440, 531)/(511, 333) to the value of u . Structures a , b , c are easily

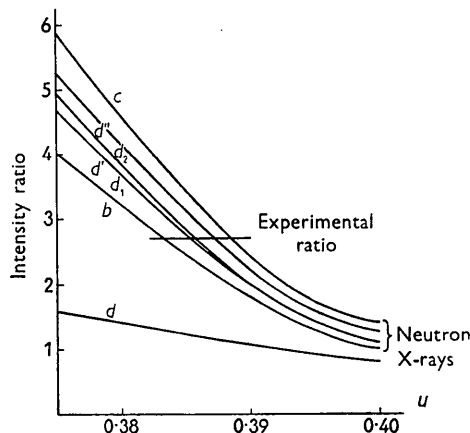


Fig. 4. MgFeAlO_4 : the calculated variation of the ratio of the neutron diffraction intensities of the pairs of lines (440, 531) and (511, 333) as a function of the oxygen parameter u , together with the observed experimental ratio.

Also shown is the calculated curve for X-ray diffraction by the structure d .

discounted by comparing intensities in Fig. 3 and it is then deduced from Fig. 4 that $u = 0.385 \pm 0.002$. In order to emphasize the particular sensitivity of the neutron intensities to the value of u a comparable curve for the structure d for X-rays is also included. Table 3 summarizes the calculated low-angle intensities for the various structures, at their slightly different optimum u values, and also gives the experimental values after a small correction has been made for thermal vibrations, again assuming $\Theta = 500^\circ\text{K}$.

Inspection of Table 3 shows that structures a , b and c may be ruled out at once, as has already been mentioned from consideration of Fig. 3. It is mentioned here that the conclusion of Nicks (1951), reported by Fairweather, Roberts & Welch (1952), that X-ray intensity measurements favour structure c cannot be justified. It arises through errors in calculation of the structure factors, in particular by neglect of the sine terms. In fact the X-ray intensities are strongly in favour of the structure d , rather than a , b or c , but are not able to distinguish between d_1 , d_2 , d' , d'' .

Returning to our consideration of Table 3 we can also discount structures d_2 and d'' , in which all the magnesium ions are in B sites, largely on the basis of the discrepancy in the intensity of the (111) reflexion which is able to discriminate the most closely between magnesium and aluminium ions. Agreement is best with structure d' , which is the structure proposed by Jones & Roberts from their magnetic results, although the neutron diffraction results alone would scarcely be able to choose this structure rather than the completely inverse arrangement d_1 .

The additional data obtained from the low-temperature diffraction pattern at -150°C . are listed in Table 4.

As for the case of MgFe_2O_4 , the magnetic scattering is negligible compared with the nuclear contribution except for the (111) and (220) reflexions and in the present instance these are reduced by a factor of four times relative to MgFe_2O_4 on account of the halving of the number of iron ions in MgFeAlO_4 .

Comparison of the magnetic contribution to (111) with that calculated for structure d' suggests that at -150°C . the magnetic alignment is sufficient to give a fraction 0.54 ± 0.11 of the maximum neutron intensity. This is to be compared with an expected value of 0.47 ± 0.08 deduced from Jones & Roberts's magnetic measurements.

Table 4. *Magnetic scattering data for MgFeAlO_4*

Reflexion	Experimental intensity		Magnetic contribution difference (-150°C .) - (20°C .)	Calculated magnetic intensity for complete alignment
	20°C .	-150°C .		
(111)	18 ± 4	58 ± 4	40 ± 8	74
(220)	77 ± 4	82 ± 4	5 ± 8	18
(311, 222)	292 ± 5	287 ± 5	-5 ± 10	7
(400)	247 ± 5	237 ± 5	-10 ± 10	9

Conclusion

The neutron diffraction results are found to support the conclusions of Jones & Roberts. In particular, they offer direct structural evidence that the MgFe_2O_4 sample is incompletely inverted and also that the aluminium ions in MgFeAlO_4 are, certainly very largely, in B sites. It is thus possible to explain the steady variation of unit-cell dimensions (Nicks, 1951) as aluminium is substituted for iron in MgFe_2O_4 . The Al^{3+} ions in these mixed ferrites enter the B sites, causing progressive reversion of Mg^{2+} into A sites. The final product is MgAl_2O_4 which, as always assumed and recently demonstrated directly by neutron diffraction (Bacon, 1952), has a 'normal' structure with Al^{3+} in B sites.

The present study arose as part of an investigation of certain ferrites at the Post Office Research Station, Dollis Hill, and was carried out at the Atomic Energy Research Establishment, Harwell.

The authors are indebted to the Director of the Atomic Energy Research Establishment and to the

Engineer in Chief of the Post Office Engineering Department for permission to publish this paper. They acknowledge the assistance of Mr R. F. Dyer and Mr N. A. Curry, of A.E.R.E., with the experimental and numerical work.

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The X-ray Scattering from a Hindered Rotator. II

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(Received 21 July 1952)

The Laue-Bragg scattering from a group of atoms undergoing hindered rotation has been derived for a generalized potential function; this should permit treatment of a non-sinusoidal potential function as well as the non-classical rotator provided its probability distribution is known. The diffuse scattering from a hindered rotator is derived, and shown to be very sensitive to the degree of hinderance. A method of deriving the scattering from a spacially hindered rotator is also presented.

Introduction

The amplitude of Laue-Bragg scattering has previously been derived (King & Lipscomb, 1950) for hindered rotation of an atom, or group of atoms, about a fixed axis. A simple sinusoidal potential function was used for which the constants refer to each individual atom. It is useful to generalize the potential function to express the potential of the rotating group as a whole, and in order to provide for non-sinusoidal potential functions. The amplitude of Laue-Bragg scattering has been calculated for this more general potential function, assuming a classical rotator with Maxwell-Boltzmann distribution in the probability function of the rotation angle. A method of using this potential function in order to include the

case of a distribution of quantum-mechanical rigid rotators is suggested.

The diffuse scattering from a hindered rotator has not previously been studied theoretically. The development indicated in the second part of the present paper for the case of a simple sinusoidal potential function indicates that the diffuse scattering should be very sensitive to the hindering potential, and quite different from that of a free rotator or that from atoms in fixed positions.

In the third part of this paper a general expansion is given which simplifies discussion of the spacially hindered rotator. Fortunately, most known examples

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