Neutron Diffraction Investigation of the Magnetic Order in MnI_2

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Neutron diffraction measurements were made on polycrystalline and single crystal samples of anhydrous MnI_2 at sample temperatures from 298°K to 1.3°K. The results show an unusual type of antiferromagnetic order below the Néel temperature of 3.40°K for this hexagonal layer type crystal. The indicated magnetic structure is a helical type in which the moments within (307) planes are aligned ferromagnetically but rotate by $2\pi/16$ in successive (307) planes. This structure is supported both by intensity measurements of the antiferromagnetic reflections and by the domain transformations effected with an applied magnetic field.

INTRODUCTION

MANGANOUS iodide crystallizes in an hexagonal layer structure of the CdI_2 type. The unit cell contains one molecule with the manganese ion located at (0,0,0) and the iodide ions at $\pm(\frac{1}{3},\frac{2}{3},u)$. Values of $u=0.245\pm0.002$, $a_0=4.146$ A, and $c_0=6.829$ A were determined for the samples used in this investigation. This structure is isomorphous with that of $MnBr_2$ and similar to that of $MnCl_2$, both of which become antiferromagnetic at low temperatures.[1] The magnetic susceptibility shows a slight departure from a Curie-Weiss dependence at liquid hydrogen temperatures and a small negative paramagnetic Curie temperature.[2] It was expected that MnI_2 would also order antiferromagnetically in the liquid helium temperature region, and this investigation represents an attempt to determine the existence and type of that magnetic order.

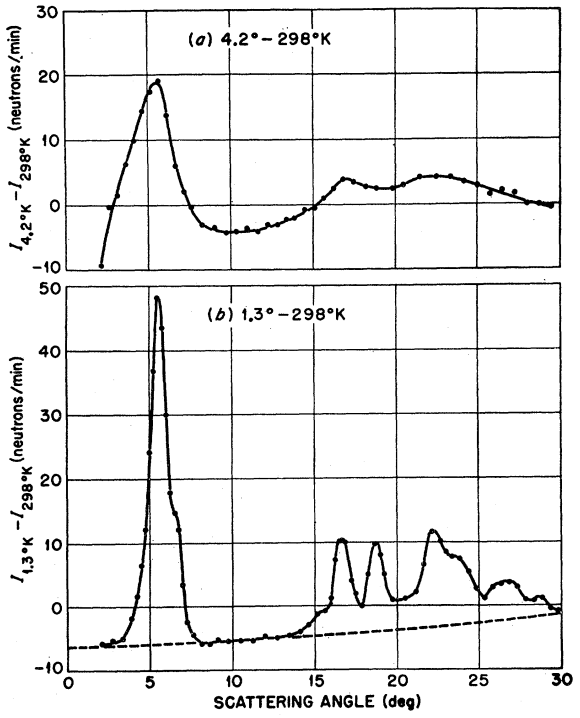

FIG. 1. Temperature difference patterns for MnI_2.

POLYCRYSTALLINE RESULTS

The preliminary data were obtained with a polycrystalline sample which was prepared by the vacuum sublimation of the anhydrous material. The sample was enclosed in a cylindrical aluminum cell which was open to the coolant chamber, so that the sample was in direct contact with the helium bath during the low temperature runs. Neutron diffraction patterns were taken at sample temperatures of 298°K, 4.2°K, and 1.3°K, and at a neutron wavelength of 1.222 A. The room temperature pattern was characteristic of a paramagnetic material, for which all of the magnetic scattering is contained in the diffuse background, and the intensities of the nuclear Bragg reflections were consistent with the known crystal structure and scattering amplitudes. At helium temperatures, coherent magnetic scattering was observed, and this is shown in the temperature difference patterns of Fig. 1. The magnetic scattering at 4.2°K is represented in curve (a), which is typical of a material in which only short range order is present. The positions and intensities of the peaks indicate an appreciable amount of antiferromagnetic short range order at this temperature. Application of the standard expression for particle size broadening to the width of the small angle peak yields an average diameter of about 22 A for the clusters of ordered moments. As the sample is cooled this small angle reflection becomes sharper and more intense. Below 3.48°K there is an abrupt intensity increase corresponding to the onset of long range antiferromagnetic order. Because of the uncertainty in the amount of short range order background below the transition, this observed transition temperature must be regarded as only approximate. A more accurate value of 3.40°K was determined with single crystal measurements for which the short range order scattering was much less pronounced.

On cooling to 1.3°K the results shown in curve (b) of Fig. 1 were obtained. The negative background, approximated by the dashed curve, corresponds to the decrease in the paramagnetic diffuse scattering from the ordered state. To a first approximation this decrease is proportional to the square of the ordered moment, and

[1] M. K. Wilkinson, Suppl. J. Appl. Phys. **30**, 278S (1959).
[2] W. J. De Haas, B. H. Schultz, and J. Koolhaas, Physica **7**, 57 (1940).

corresponds to a value of $(4.6\pm0.5)\mu_B$ per Mn^{+2} ion. The reflections in this pattern were not well resolved and could not be indexed on any simple magnetic unit cell. It was decided to extend the investigation to single crystal samples.

SINGLE CRYSTAL RESULTS

The single crystals were grown from a melt of the anhydrous material by the Bridgman technique. The sample specimens were cut in the shape of flat cylinders about $\frac{1}{4}$ in. in diameter and $\frac{1}{8}$ in. thick with the (00*l*) natural cleavage planes forming the flat ends of the cylinder. The specimens were mounted in the low temperature goniometer[3] with the *c* axis of the crystal parallel to the horizontal rotation axis of the goniometer. In the low temperature runs the crystal was in direct contact with the helium bath, and sample temperatures were measured with a calibrated carbon resistor.

On examination of the nuclear reflections from these crystals it was apparent that they contained secondary grains which were rotated 60° about the *c* axis with respect to the primary grains. This type of crystal growth is not unexpected in these crystals because of the weak interlayer forces and consequent ease of introduction of stacking faults. The presence of these secondary grains does not affect the intensities of those reflections with axial or sixfold symmetry, such as the (00*l*) and (*hhl*) reflections, but appreciably alters the intensities of the (*h*0*l*) and *hkl*) reflections which have only three-fold symmetry. From the relative intensities of the latter it was possible to determine the fraction of the crystal in each grain. The magnetic reflections are also affected by these stacking faults; and, for these, it was possible to resolve the scattering from the two grains. Thus, the intensity of any magnetic reflection relative to its counterpart, obtained by rotation of the crystal by 180° about the *c* axis, was a direct measure of the fraction of the crystal in each grain. The values obtained in this way agreed with those taken from the nuclear intensities. After the examination of several crystals, all of which showed the presence of secondary grains to an extent of 10% to 30% of the crystal, it was decided to abandon the search for a real single crystal and proceed with a crystallographically impure specimen. Two specimens were chosen, on the basis of peak shape and reflectivity, for which 10% and 27% of the crystal was contained in the secondary grain. The intensity measurements and the analysis of the data were performed on the primary grain of each specimen.

The larger 73% primary grain crystal was examined in detail in the magnet spectrometer with a neutron wavelength of 1.075 A. A less detailed examination of the other crystal was performed at a neutron wavelength of 1.222 A. Consistent results were obtained, but only the more detailed examination is described in the following paragraphs.

[3] E. O. Wollan, W. C. Koehler, and M. K. Wilkinson, Phys. Rev. **110**, 638 (1959).

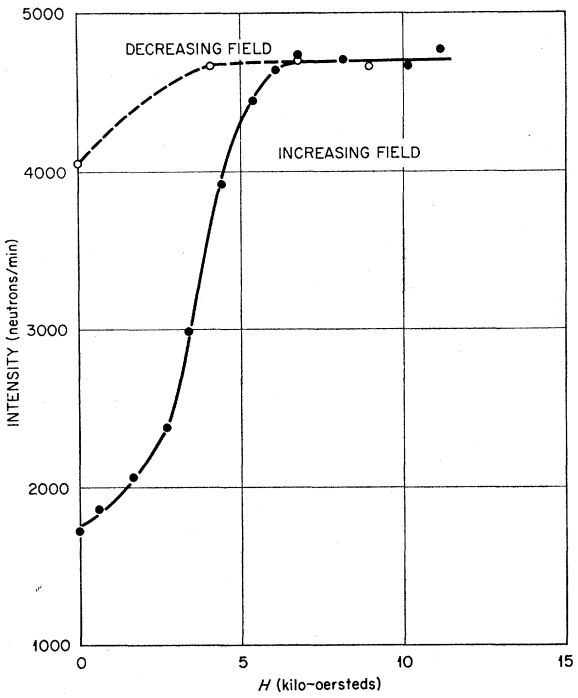

FIG. 2. Field dependence of the (000^+) reflection of MnI_2.

The small angle magnetic reflection observed in the powder data was the first to be studied, and this reflection appeared at the same azimuthal angle about the *c* axis as the (*h*0*l*) nuclear reflections. Several other magnetic reflections were found at the same angle but with smaller *d* spacings and different angles between the scattering vectors and the *c* axis. All of these reflections exhibited three-fold symmetry about the *c* axis. In the previous studies of $MnCl_2$ and $MnBr_2$ threefold symmetry was also observed, but was shown to be a property of the domain growth rather than of the magnetic unit cell. This was demonstrated by the application of a magnetic field to the sample in the ordered state. It was found that the threefold symmetry was destroyed and the intensity of a given reflection enhanced by a factor of three when the field was applied in the proper direction. This effect could not be explained by a moment rotation within a magnetic unit cell of threefold symmetry, but rather required a domain transformation interpretation. According to this interpretation there are antiferromagnetic domains which, in the absence of a magnetic field, grow with equal probability along three equivalent hexagonal axes. Application of a magnetic field favors that domain with moments most nearly perpendicular to the field direction. This domain grows at the expense of the other two until at saturation the entire crystal is transformed into a single domain. This results in the enhancement of the intensity of any magnetic reflection from that domain by a factor of three and the destruction of the threefold symmetry. This experiment was performed on the MnI_2

single crystal at 1.38°K with the magnetic field applied parallel to the scattering vector of the small angle magnetic reflection, and the result is shown in Fig. 2. The intensity increases with increasing field until at 6 koe saturation is achieved with an intensity increase of a factor of 2.7. This actually corresponds to complete transformation to a single domain because even in zero field this particular reflection contained 37% of the total intensity from the three domains. On removal of the field, about 80% of the enhanced intensity remained. The crystal was then rotated to the other two symmetry related reflections and they were essentially extinguished, which showed the destruction of the three-fold symmetry. This experiment showed that the actual magnetic unit cell had only onefold symmetry and that the apparent three-fold symmetry was a domain growth property of the system.

The field-induced single domain crystal was used in the search for additional magnetic reflections and to check the reflections predicted by various models. The observed magnetic reflections can best be described with the aid of a reciprocal space diagram as shown in Fig. 3. In this diagram b_1 and b_3 are reciprocal lattice vectors of the chemical unit cell, and reciprocal lattice sites are designated by appropriate indices. The open circles represent the location of the observed magnetic reflections in this plane of reciprocal space. The vector τ describes the displacement of the magnetic reflection denoted by (000^+) from the origin. Notice that all of the magnetic reflections in this plane of reciprocal space can be described by either adding or subtracting the vector τ to the reciprocal lattice vectors of the chemical cell. The magnetic reflections can then be indexed as $hkl^{\pm}$ as shown in the diagram with the positive sign indicating addition to, and the negative sign subtraction from, the reciprocal lattice vectors of the chemical cell. This was observed not only for this plane but throughout the region of reciprocal space examined. The scattering vector, ϵ_{hkl}, of a magnetic reflection is given by: $\epsilon_{hkl}=B_h\pm\tau$, where $B_h=b_1h_1+b_2h_2+b_3h_3$ and $\tau=(3b_1+7b_3)/16$. The physical interpretation of these observations is straightforward even though the resultant description of the magnetic ordering can become quite complex. The vector τ is the wave vector of the modulation of the magnetic scattering amplitude. From the direction and magnitude of τ one concludes that the moments within (307) planes are ferromagnetically

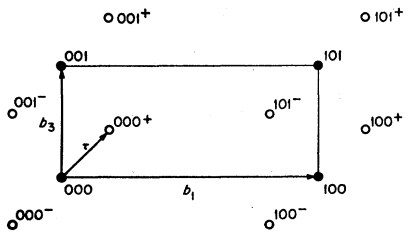

FIG. 3. Magnetic scattering density in reciprocal space for MnI_2.

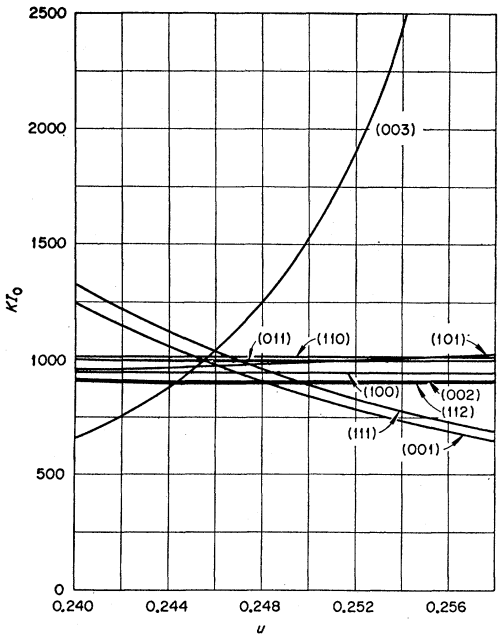

FIG. 4. The graphical determination of the instrumental constant, KI_0.

aligned and are periodically in phase every 16 such planes. The complexity of the problem arises when a description of the modulation is attempted. The two simplest cases are: (1) A helical structure such as that described for[4] MnO_2 and[5] $MnAu_2$ and (2) An antiphase domain type structure such as that originally proposed for Cr.[6] In the helical type structure the moments lie in some plane (not necessarily the (307) plane in which they are ferromagnetically aligned) and rotate by $2\pi/16$ in subsequent (307) planes proceeding along the direction of τ. In the antiphase domain structure the moments within the (307) planes are all aligned parallel to the magnetic axis with an abrupt reversal of direction every eight planes. This then corresponds to square wave modulation as opposed to sine wave modulation for the helix. Either model yields magnetic reflections in the observed positions, but with quite different intensities.

In order to obtain absolute intensity measurements it is necessary to evaluate the instrumental constant, KI_0 in the expression for the integrated intensity, E_{hkl}, of an (hkl) reflection from a single crystal:

$$E_{hkl}=KI_0F_{hkl}^2e^{-2w}A_{hkl}/\sin 2\theta.$$

In this expression θ is the Bragg angle, F_{hkl} is the structure amplitude, A_{hkl} is an absorption correction, and the exponential term is the Debye-Waller factor. In this analysis of the magnetic intensities A_{hkl} was in-

[4] A. Yoshimori, J. Phys. Soc. Japan 14, 807 (1959).
[5] A. Herpin, P. Meriel, and J. Villain, Compt. rend. 249, 1334 (1959).
[6] L. M. Corliss, J. M. Hastings, and R. J. Weiss, Phys. Rev. Letters 3, 211 (1959).

TABLE I. Comparison of the calculated and observed absolute intensities of the antiferromagnetic reflections from MnI_2.

$hkl^{\pm}$	F_{hkl}^2 (calc)[a]	F_{hkl}^2 (obs)	$hkl^{\pm}$	F_{hkl}^2 (calc)[a]	F_{hkl}^2 (obs)
000^+	0.72	0.69	010^+	0.27	0.27
001^-	0.39	0.33	011^-	0.29	0.29
001^+	0.51	0.43	011^+	0.27	0.29
002^-	0.37	0.41	012^-	0.28	0.23
002^+	0.31	0.30			
003^-	0.24	0.29	$1\bar{1}0^+$	0.27	0.28
			$1\bar{1}1^-$	0.29	0.29
100^+	0.31	0.35	$1\bar{1}1^+$	0.27	0.27
101^-	0.46	0.49	$1\bar{1}2^-$	0.28	0.25
101^+	0.29	0.29			
102^-	0.41	0.44	$\bar{1}10^+$	0.25	0.24
			$\bar{1}11^-$	0.22	0.23
$\bar{1}00^+$	0.29	0.34	$\bar{1}11^+$	0.22	0.20
$\bar{1}01^-$	0.23	0.29	$\bar{1}12^-$	0.16	0.16
$\bar{1}01^+$	0.22	0.24			
$\bar{1}02^-$	0.15	0.17	$0\bar{1}0^+$	0.25	0.24
...	...	...	$0\bar{1}1^-$	0.22	0.24
...	...	...	$0\bar{1}1^+$	0.22	0.19
...	...	...	$0\bar{1}2^-$	0.16	0.18

[a] Assuming 4.6 μ_B/Mn^{+2} ion, the Mn^{+2} form factor, and that the plane containing the moments is normal to the helical axis.

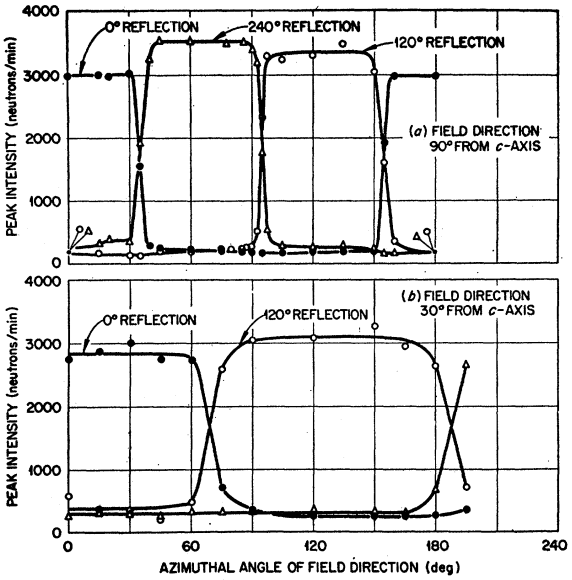

FIG. 6. The angular dependence of the field induced domain transformations in MnI_2.

corporated into the instrumental constant, KI_0, which was determined from the nuclear intensities and then applied to the magnetic intensities. The determination of KI_0 is shown in Fig. 4 in which the abscissa is the positional parameter of the iodide ions. Each curve gives the value of KI_0 required to account for the observed intensity as a function of this parameter u. The intersection of the curves gives the values of KI_0 and u which satisfy the above expression for all of the observed nuclear intensities. The spread in KI_0 at the intersection shows that absorption and extinction effects are, within 10%, the same for all of the reflections observed.

In the antiphase domain model, or any other model with a single magnetic axis, the magnetic intensities are proportional to $q^2=1-(\boldsymbol{\varepsilon}\cdot\mathbf{k})^2$ in which $\boldsymbol{\varepsilon}$ and $\mathbf{k}$ are unit vectors parallel respectively to the scattering vector and the magnetic axis. Whatever direction that $\mathbf{k}$ assumes, there will be some magnetic reflections for which the scattering vectors make small angles with $\mathbf{k}$ and which should therefore have very low intensities. For the simple helical structure there is no unique magnetic axis and the intensity of magnetic scattering is proportional to $(1+\cos^2\varphi)/2$, in which φ is the angle between the scattering vector and the normal to the plane containing the moments.[7] For such a structure the absolute intensities cannot vary by more than a factor of two (exclusive of the form factor) regardless of the direction of the normal to the plane of the moments, or the direction of the scattering vector.

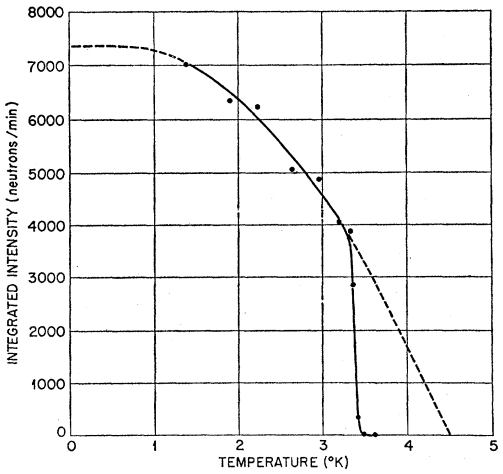

FIG. 5. Temperature dependence of the (000^+) reflection of MnI_2.

For MnI_2, the intensities of the reflections in various directions cannot be explained on any model with a single magnetic axis, but are in accord with the simple helical model. This is shown in Table I in which the reflections are indexed in the previously described manner. In calculating the structure factors, the Mn^{+2} form factor and a moment of 4.6 μ_B per Mn^{+2} ion were used. The plane containing the moments was assumed normal to the helical axis. Agreement is obtained to about 10% for most of the reflections with a few discrepancies approaching 20%. This agreement is comparable to that observed for the nuclear reflections and strongly suggests the helical moment configuration for MnI_2.

The previously mentioned transition temperature determination is shown in Fig. 5 in which the intensity of the (000^+) reflection is plotted versus temperature. The transition at 3.40°K from short range to long range antiferromagnetic order is unusually sharp. This is emphasized by the dashed curve which corresponds to the type of temperature dependence usually observed

[7] W. C. Koehler, Acta Cryst. 14, 535 (1961).

for such cooperative phenomena. Associated with this abrupt transition to the state of long range order is a large amount of short range order above the transition. The unusually sharp dependence of the ordering energy on the amount of local order already present is probably due to the existence of interactions over several near neighbor distances.

FIELD EFFECT

As shown in Fig. 2 a magnetic field of 6 koe applied parallel to the scattering vector of the (000+) reflection at a temperature of 1.3°K is sufficient to convert the entire crystal into a single domain. It was also observed that only a small fraction of the crystal reverts to the other two domains when the field is removed. This remanent domain effect enables one to observe the domain behavior as a function of the direction of application of the field. This was done in the following way. In zero field there are three (000+) reflections, corresponding to the three domains, and these occur in 120° intervals about the c axis of the crystal. The intensities of these reflections were measured after a magnetic field of 10 koe had been applied and removed. Successive measurements were made with a constant angle between the field direction and the c axis and a stepwise variation in the angle about that axis. The results are shown in Fig. 6 in which the abscissa refers to the angle about the c axis at which the field was applied and the (000+) reflections are designated in the same coordinate system. In curve (a) the field was applied normal to the c axis, and each of the three domains is favored for one third of the 360° rotation about that axis. The favored region for a given domain consists of two 60° intervals centered on the axis corresponding to that domain growth direction. For example, the reflection observed at an azimuthal angle of 0° is enhanced by the application of the field in the angular region 30° either side of 0° and also in the region 30° either side of 180°. A different result was obtained when the field was applied out of the (00l) plane, and this is illustrated in part (b) of Fig. 6. In this case the field was applied at an angle of 30° with respect to the c axis, and the cone of revolution of the field direction closely approaches the scattering vectors of the three (000+) reflections. Each domain is again favored for one third of the complete rotation about the c axis, but now the favored region for a given domain consists of a single 120° angular interval centered about the axis of domain growth.

In antiferromagnetic materials an externally applied magnetic field favors that domain in which the moments are most nearly normal to the field direction. It is extremely difficult to interpret these results on the basis of a magnetic structure with a single magnetic axis per domain. They are, however, precisely the results expected for the helical model in which the magnetic moments lie in planes normal to the axis of the helix, and for which the field induced domain transformations are dependent only on the angle between the helical axes and the field direction. Since this is also the model which yields agreement with the observed intensities, the field effects support that model as the correct magnetic structure.

DISCUSSION

The intensity measurements of the antiferromagnetic reflections from MnI_2 indicate a helical magnetic structure in which the moments are ferromagnetically aligned in (307) planes, lie within those planes and rotate by $2\pi/16$ in successive (307) planes. Additional support for this structure is obtained from the field induced domain transformation properties. Theoretical treatments[4,8] have shown that helical structures are energetically stable for certain ratios of the exchange integrals for three near neighbor interactions, and such structures are consistent with neutron diffraction data obtained for MnO_2,[4] $MnAu_2$,[5] Ho,[9] Dy,[10] and Er.[11] In all of these cases the helical axis was parallel to the unique crystal axis, and the relevant near neighbor interactions could be readily visualized. In the present case the helical axis assumes a direction which has no apparent correlation with the near neighbors. Consequently, it is not clear which of the near neighbor interactions are important in this crystal.

ACKNOWLEDGMENT

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[8] J. Villain, J. Phys. Chem. Solids **11**, 303 (1959).
[9] W. C. Koehler, J. W. Cable, E. O. Wollan, and M. K. Wilkinson, Bull. Am. Phys. Soc. **5**, 459 (1960).
[10] M. K. Wilkinson, W. C. Koehler, E. O. Wollan, and J. W. Cable, Suppl. J. Appl. Phys. **32**, 48S (1961).
[11] J. W. Cable, E. O. Wollan, W. C. Koehler, and M. K. Wilkinson, Suppl. J. Appl. Phys. **32**, 49S (1961).