

Evans⁶ obtained 4×10^{-30} cm² per nucleon for the cross section for production of shower particles (which were probably also π -mesons with energies $> 10^8$ ev) by μ -mesons of energy $\sim 10^{10}$ ev. Therefore, there is no rapid increase in the cross section for high energy

⁶ E. P. George and J. Evans, Proc. Phys. Soc. (London) **63**, 1248 (1950).

nuclear interactions with increasing energy of μ -mesons. If we again consider the specific process of photomeson production, the cross section $\sigma(\nu, \pi^{+-})$ is less than 10^{-28} cm² per nucleon, which again is not surprising.

Cooperation by the management and personnel of the International Salt Company Detroit Mine made this work possible.

Neutron Diffraction Study of the Crystal Structure of Ammonium Chloride*

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The crystal structure of the room-temperature phase of ammonium chloride has been determined by powder and single crystal neutron diffraction methods. The N—H links are directed essentially toward four of the eight surrounding chloride ions, and, contrary to a recent report, the two orientations fulfilling this condition are occupied at random in the crystal. Thermal motion of the hydrogen atoms is nonspherical and suggests a rotatory oscillation of the ammonium ion as a whole with a half-angle of about 10°. The length of the N—H link is 1.03 ± 0.02 Å. The second-order transition at -30°C is thus shown to be of the order-disorder type.

INTRODUCTION

AMMONIUM chloride undergoes a second-order transition at -30.4°C , and deuterio-ammonium chloride undergoes one at -23.7°C , the nature of which has been the subject of much experimental and theoretical study.¹ The most recent of these studies is a neutron diffraction investigation of the crystal structure of this substance at room temperature and at liquid nitrogen temperature, carried out by Goldschmidt and Hurst.² These investigators report that at both temperatures the structure consists of an ordered array of ammonium and chloride ions conforming to space group symmetry T_d^1 , the room temperature phase differing from the other only in displaying greatly increased motion of the hydrogen atoms of a sort that can be described as a rotatory oscillation of the ammonium ions.

This reported room-temperature structure contrasts sharply with that found by us, also by neutron diffraction for room-temperature ammonium bromide.^{3,4} The ammonium bromide structure was found to conform statistically to space group symmetry O_h^1 and to contain ammonium ions oriented at random in two orientations with hydrogen atoms directed essentially toward four of the eight surrounding bromide ions. This

significant feature of the ammonium bromide structure confirms the suggestion of Nagamiya⁵ concerning the specific nature of the transition and might reasonably be expected to be a characteristic feature of the structures of other ammonium halides which display second-order transitions. Thus it is of some importance to have an independent check on the ammonium chloride result.

The methods used in the present investigation of ammonium chloride consist of both powder and single crystal studies using neutron diffraction techniques. It was considered essential to repeat the work of Goldschmidt and Hurst using a deuterated powder sample. In addition, since single crystal neutron diffraction techniques have been shown to be feasible,⁶ they were also employed. Data obtained by the latter method were particularly decisive in establishing the correct structure, which consists of orientationally disordered ammonium ions altogether similar to that found in room-temperature ammonium bromide.

POWDER DATA FROM ND_4Cl

Experimental

The general design of the spectrometer and associated circuits is similar to that of Wollan and Shull⁷ and will be described elsewhere. The monochromatic beam was produced by reflection from a (111) face of a copper crystal and yielded a wavelength of 1.16Å, which was used in both the powder and single crystal work.

* This work was performed for the AEC.

¹ Previous work is summarized by E. L. Wagner and D. F. Hornig, J. Chem. Phys. **18**, 296 (1950), and in reference 2.

² G. H. Goldschmidt and D. G. Hurst, Phys. Rev. **83**, 88 (1951). (This will be referred to as G. and H.)

³ H. A. Levy and S. W. Peterson, Phys. Rev. **83**, 1270 (1951).

⁴ H. A. Levy and S. W. Peterson, "The crystal structures of four phases of deuterio-ammonium bromide by neutron diffraction," J. Am. Chem. Soc. (to be published).

⁵ T. Nagamiya, Proc. Phys. Math. Soc. Japan **24**, 137 (1942).

⁶ S. W. Peterson and H. A. Levy, J. Chem. Phys. **19**, 1416 (1951); G. E. Bacon, Proc. Roy. Soc. (London) **A209**, 397 (1951).

⁷ E. O. Wollan and C. G. Shull, Phys. Rev. **73**, 830 (1948).

Deutero-ammonium chloride was prepared by repeated recrystallization of reagent grade ammonium chloride from 99.8 percent D_2O . The resulting product had a deuterium content of 98 mole percent, established as described elsewhere.⁴ The sample was handled under dry box conditions and exposed to the neutron beam in tightly sealed cylindrical aluminum cells. A number of runs were made at room temperature on the same deuterated powder sample with varying degrees of collimation in the neutron detector. Runs were also made at dry ice and liquid nitrogen temperatures in order to look for any anomalous behavior; they yielded essentially identical patterns and intensities in good agreement with those of Goldschmidt and Hurst at liquid nitrogen temperature.

X-ray studies of NH_4Cl at room temperature have shown the structure to be of the CsCl type with a unit cell length of 3.866 Å.⁸ The neutron diffraction pattern from deuterated ammonium chloride was consistent with the above structure and spacing and was indexed on this basis. A typical room-temperature pattern is illustrated in Fig. 1. It was evident that the background of diffuse scattering is angle-dependent, its most prominent feature being a hump in the neighborhood of 40° scattering angle. Integrated intensities were obtained directly from chart records of the diffracted counting rate, after fixing the estimated background rate as illustrated in the figure, by application of the trapezoid rule. When necessary, corrections were made

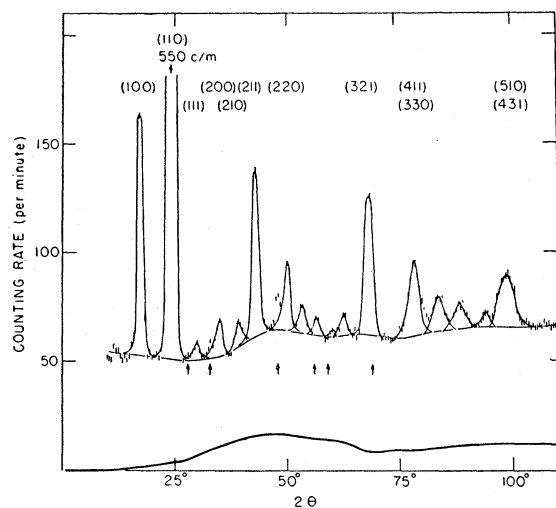


FIG. 1. The neutron diffraction pattern of room-temperature deutero-ammonium chloride. The short vertical lines represent the observed counting rate and the precision of reading from the original strip-chart records. The uppermost curves show the principal Bragg reflections as they would be idealized on the original charts for intensity estimation. The undulating curve through the base of the pattern is the estimated background. The lower curve is the calculated disorder scattering. Arrows indicate angles at which appreciable scattering by aluminum occurs.

⁸ R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1951), Vol. I, Chapter III, table p. 23.

TABLE I. Comparison of data and calculated structure factors for ND_4Cl .

hkl	Experimental $ F $		Calculated $ F $	
	G. and H.	This research	Ordered ^a	Disordered ^b
100	$1.41 \pm 2\%$	1.33 ± 0.03	1.41	1.31
110	$2.47 \pm 2\%$	2.48 ± 0.06	2.48	2.52
111	$0.89 \pm 5\%$	0.37 ± 0.07	0.95	0.33
200	$1.09 \pm 20\%$	0.96 ± 0.09	1.11	1.02
210	$0.68 \pm 20\%$	0.39 ± 0.07	0.56	0.44
211	$1.43 \pm 20\%$	1.36 ± 0.06	1.54	1.32
220	$1.39 \pm 20\%$	1.40 ± 0.15	1.25	1.56
222	$1.08 \pm 40\%$	1.14 ± 0.20	1.54	1.31
321	$1.32 \pm 5\%$	1.50 ± 0.08	1.28	1.45

^a From reference 2.

^b For the final model described in the text.

for scattering by the empty sample container. Final values were averages of those from several patterns. Values of jF^2 were obtained in the usual way, the instrument-beam parameter being evaluated by comparison with nickel powder ($\sigma_{\text{coh}}(\text{Ni}) = 13.4$ barns).

Direct comparison of our neutron diffraction pattern and resulting intensities with those of G. and H. (see Table I) makes evident a considerable disagreement in the range of reflections from (111) through (211) and (321). The large discrepancy in the (111) reflection is of especial significance because of the importance placed on this reflection by G. and H. in their structure analysis. We have made repeated measurements of this reflection and have in no case obtained an intensity which was close to their value. It seems likely that a different estimate of the background counting rate on the part of G. and H. is at least partly responsible for the disagreements. It may well be that when intensities of imperfectly resolved reflections are estimated from an integral curve, as was done by G. and H., proper background treatment is difficult and variations in background are obscured.

We have recently been informed that Dr. Hurst has remeasured neutron diffraction intensities from ND_4Cl and now obtains relative values of the structure factors in agreement with ours.[†]

Structure Determination

In view of the earlier neutron studies of ND_4Cl and ND_4Br the only models considered here are those involving ordered and disordered ammonium ion arrangements, space groups T_d^1 and O_h^1 , respectively. Nitrogen is placed at the origin and bromine at the body center in both models. In the ordered model the hydrogens are centered at the fourfold positions $x x x$, $x \bar{x} \bar{x}$, $\bar{x} x x$, and $\bar{x} \bar{x} \bar{x}$; in the disordered model hydrogens are distributed at random between this set of positions and the remainder of the eightfold set obtained by inversion through the origin. In both models non-spherical distribution of the hydrogen atoms was considered, such as would result from a rotatory oscil-

[†] Dr. Hurst's new measurements are described elsewhere in this issue.

TABLE II. Powder neutron diffraction data for ND₄Cl.

<i>hkl</i>	Obs	<i>j F </i> ² Calc ^a	<i>hkl</i>	Obs	<i>j F </i> ² Calc ^a
100	10.6±0.3	10.3	400	<3.3	0.5
110	74.0±3.5	75.9	410	7.4±5.4	{4.9
111	1.1±0.5	0.85	322		{0.0
200	5.5±1.1	6.2	411	71±26	{17.4
210	3.6±1.5	4.6	330		{45.1
211	43.4±5.0	41.6	331	<10.8	5.5
220	23.6±5.8	29.2	420	45±13	39.5
221	12.0±3.0	{0.0	421	<8.6	1.3
300		{14.1	332	<25.6	12.8
310	<9.1	7.1	422	<20.1	15.7
311	<5.5	5.4	500	<14.9	{0.0
222	10.4±4.0	13.7	430		{6.3
320	<3.0	2.7	510	83±21	{18.6
321	108±12	100.2	431		{56.0

^a For the final (disordered) model described in the text.

lation of the ammonium ion as a whole. Structure factors were calculated for both models with the ideal position parameter x and the characteristic half-angle of rotatory oscillation α as principal parameters. The effect of rotatory oscillation was approximated in the same way as in our treatment of room-temperature ammonium bromide,⁴ in which the expressions used to approximate the structure factors are given. Separate temperature factors for each of the atoms were introduced as additional parameters. Trial and error calculations were continued until it was seen that no fit could be obtained with the ordered model, and a satisfactory best fit was found for the disordered model. The parameter values found to give the best fit are

$$x = 0.154 \pm 0.003, \quad \alpha = 10^\circ \pm 3^\circ,$$

$$B_D = 2.25, \quad B_N = 2.0 \text{ and } B_{Cl} = 2.0.$$

Table I gives the experimental and calculated structure factors of Goldschmidt and Hurst as compared with similar values obtained for the same reflections in this work. The ($hk0$) reflections are not sensitive to whether the ordered or disordered model is used; variations in these values between columns 4 and 5 of the table arise from different values of atomic scattering factors and temperature factors and slightly different approximations in treating the effects of rotatory oscillation. The remainder of the calculated values reflect also the effect of ordered or disordered structure. The atomic scattering factors used here were in units of 10^{-12} cm, $f_N = 0.94$,⁹ $f_{Cl} = 0.99$,¹⁰ and $f_{D,H} = 0.62$ ¹⁰ (for 98 percent D, 2 percent H). (The calculations were begun with $f_N = 0.85$, as measured and used by G. and H.; however, our single crystal data strongly indicated the necessity for a larger value, subsequently confirmed by measurements⁹ on VN and KN₃.)

The most significant reflection in deciding between the ordered and disordered arrangements is clearly (111) although (211), (222), and (321) also are of

⁹ H. A. Levy and S. W. Peterson, "The coherent neutron scattering cross-sections of nitrogen and vanadium" (to be published).

¹⁰ C. G. Shull and E. O. Wollan, Phys. Rev. **81**, 527 (1951).

importance. The new data presented here are clearly not compatible with the calculated values presented by G. and H., and no variation of parameters in the ordered model suffices to bring agreement. Further, the G. and H. data are, except for the controversial (111) reflection, in as good agreement, on the whole, with the disordered model as with their ordered model. The somewhat surprising result that the same N—D distance is obtained as by G. and H. is due to the necessity of fitting the strong (100) and (110) reflections which are independent of the model and, in addition, to the accidental compensating effect in their use of scattering amplitudes larger for deuterium and smaller for nitrogen and chlorine than were used in this work. The use of these somewhat different scattering amplitudes of G. and H. would not change our conclusion regarding the correctness of the disordered structure but would slightly change the parameter values giving the best fit. Table II presents experimental and calculated structure factors for the whole range of scattering angle obtainable with our present spectrometer and wavelength. Good agreement is achieved throughout for the disordered model.

Disorder Scattering

The angle dependent diffuse background might be expected to arise from the disorder in the ammonium chloride crystal structure. That this is indeed the case is indicated by an application of the general theory of disorder scattering described by Zachariasen.¹¹ If it is assumed that the orientations of the ammonium ions are statistically independent, Zachariasen's Eq. (4.216b) applies,

$$J_2 = \text{const} [\langle |F|^2 \rangle_{av} - |\bar{F}|^2],$$

in which $\langle |F|^2 \rangle_{av}$ is the mean square structure factor, \bar{F} the mean structure factor over the crystal, and J_2 is proportional to the disorder scattering. This reduces in Zachariasen's notation to

$$J_2 = \text{const} \sum_{k,k'} \varphi_{kk'}^0 \exp[i\delta \cdot (\bar{r}_k - \bar{r}_{k'})],$$

in which $\varphi_{kk'}^0$ is the mean of the product of the deviations of the scattering amplitudes at positions k and k' from the mean value, and the double sum is over the various sites in one unit cell. For our case

$$\varphi_{kk'}^0 = \pm \frac{1}{4} f_D^2$$

with a positive or negative sign according to whether k and k' designate corners of the same or different tetrahedra. Upon averaging over all orientations of the vector $\bar{r}_k - \bar{r}_{k'}$ we obtain

$$J_2(s) = \text{const} \cdot 2f_D^2 \{ 1 - 3(\sin r_1 s)/r_1 s + 3(\sin r_2 s)/r_2 s - (\sin r_3 s)/r_3 s \}, \quad (1)$$

where $s = (4\pi/\lambda) \sin\theta$ and r_1 , r_2 , and r_3 are the distances

¹¹ W. H. Zachariasen, *Theory of X-Ray Diffraction in Crystals* (John Wiley and Sons, Inc., New York, 1945), p. 213.

between deuterium sites separated by a cube edge, face diagonal, and body diagonal, respectively. In applying this expression we have included temperature factors in the same way as is usual in the case of gas scattering, namely a factor $\exp(-\frac{1}{2}\langle\delta r_i^2\rangle_{Av}s^2)$ multiplying each angle-dependent term, in which $\langle\delta r_i^2\rangle_{Av}$ is the mean square variation in distance r_i . For the distances r_1 and r_3 values of $\langle\delta r_i^2\rangle_{Av}$ were estimated from the values of B_D and α found from the Bragg scattering, while $\langle\delta r_2^2\rangle_{Av}$ was estimated from vibrational frequencies, namely ~ 2300 cm⁻¹ for stretching and ~ 1100 cm⁻¹ for bending.¹

In Fig. 1 there is plotted the function obtained when numerical values are substituted into Eq. (1), namely

$$J_2(s) = 11.37\{1 - 3 \exp(-0.04s^2)g(1.190s) + 3 \exp(-0.02s^2)g(1.682s) - \exp(-0.03s^2)g(2.061s)\},$$

where $g(x)$ represents $(\sin x)/x$. The multiplying constant was evaluated from a Bragg peak of the same pattern, so that J_2 is given in counts per minute on an absolute scale. The qualitative similarity to the observed diffuse background is striking. The remainder of the background is expected to arise from thermal scattering, nuclear diffuse scattering, and multiple scattering in the sample.

SINGLE CRYSTAL DATA ON NH₄Cl

In view of the disagreements in data in powder studies it seemed desirable to have a further independent check on the proposed structure by means of the more sensitive single crystal method. The low backgrounds and high intensities obtainable with single crystal methods eliminate large uncertainties in intensities of low angle peaks of such an intensity as (111). In addition, it is possible to work with the hydrogen compound which makes an interesting comparison with the deuterium substituted compound.

Single crystals of ammonium chloride were grown by the method of Holden¹² from a saturated aqueous solution of ammonium chloride containing approximately 10 percent of urea. Specimens of cubic habit with dimensions up to 1 cm or more on edge were easily obtained. The amount of urea incorporated is very small,¹³ and the specimens were optically very clear. Small rectangular specimens were first selected for study; however, measurements soon indicated that absorption was an important factor (apparent absorption due to large diffuse scattering). Selected specimens were then ground to cylindrical shape by slow abrasion or etching while they were rotating at a high speed in a drill press. Precise absorption corrections could then be made using the measured linear absorption coefficient, and the intensity data could be placed on an absolute scale.

TABLE III. Neutron diffraction data from NH₄Cl single crystals.

<i>hkl</i>	$ F _{\text{obs}}$	Disordered ^a	$ F _{\text{calc}}$	Ordered ^b
100	0.88±0.03	0.88		
110	1.36±0.04	1.36		
111	0.31±0.05	0.26		0.71
200	2.00±0.06	2.04		
210	0.23±0.07	0.20		
211	1.72±0.05	1.71		1.82
220	1.46±0.05	1.46		
221	<0.10	0.04		0.60
300	0.83±0.04	0.78		
310	1.81±0.06	1.82		
320	0.18±0.06	0.20		
400	1.59±0.06	1.54		
410	0.12±0.10	0.17		
330	0.62±0.04	0.63		
420	0.85±0.04	0.84		
500	<0.10	0.02		
430	0.16±0.10	0.24		
510	0.81±0.05	0.78		
520	<0.10	0.08		

^a For the final model described in the text.

^b For an ordered model, symmetry *T*_h, based on the same parameter values as the final model.

Equatorial data were obtained in a manner previously described by Peterson and Levy^{6,14} on specimens ground to cylindrical shape with [100] and [110] zone axes vertical. The weights and dimensions of the specimens were 13.0 mg, 5.3-mm high×1.4-mm diameter, and 13.6 mg, 4-mm high×1.6-mm diameter. The observed integrated reflections, corrected for absorption, were converted to absolute structure factors by use of a standard NaCl reflection.⁶ The final value used was in most cases an average of two runs. The thin crystal criterion of Bacon and Lowde¹⁵ would permit a maximum thickness with negligible extinction of 0.8 mm on the assumption of a mosaic spread parameter of 5 minutes.⁶ The somewhat larger specimens used gave no indication of extinction as shown by the following direct comparison of absolute *F* values obtained from the strongest reflections of NH₄Cl powder and from a single crystal:

<i>hkl</i>	Structure factor	
	Powder	Single crystal
100	0.90	0.88
110	1.34	1.36

The excellent agreement obtained with the proposed structure is further evidence that extinction was not a problem here.

The data obtained are presented in Table III along with calculated structure factors for the model which gave the best fit. The excellency of the over-all agreement is evidence for the validity of the structure and temperature parameters. The parameters, which were evaluated by trial and error, are $x=0.154\pm 0.003$, $\alpha=12^\circ\pm 3$, $B_N=2.0$, $B_{Cl}=2.0$, and $B_H=2.5$. The scat-

¹² A. N. Holden, Disc. Faraday Soc. No. 5, 312 (1949).

¹³ An x-ray diffraction pattern showed no urea lines.

¹⁴ S. W. Peterson and H. A. Levy, J. Chem. Phys. (to be published).

¹⁵ G. E. Bacon and R. D. Lowde, Acta Cryst. 1, 303 (1948).

tering amplitudes used were

$$f_N = 0.94,⁹ f_{Cl} = 0.99,¹⁰ \text{ and } f_H = 0.38.¹⁶$$

The three (*hkl*) reflections (111), (211), and (221) are decisive in eliminating the ordered structure, for which calculated *F* values are presented in column 4, based on the same set of parameters. The disagreements are so great that no reasonable variation of the parameters can resolve them.

A by-product of the work is evidence that the earlier value of f_N , 0.85,^{2,10} is incorrect and that a scattering amplitude for hydrogen of 0.38¹⁶ is to be preferred to the earlier value of 0.40.¹⁰ The (100) reflection which is quite sensitive to the hydrogen amplitude and little affected by the temperature and structure parameters is most significant in this respect.

DISCUSSION

The data presented establish clearly that the room temperature structure of NH_4Cl involves a disorder in the orientation of the ammonium ions. This is in agree-

¹⁶ Hughes, Burgy, and Ringo, *Phys. Rev.* **77**, 291 (1950).

ment with less direct evidence.¹ Since the low temperature structure of ammonium chloride is clearly an ordered one, the lambda-transition is of the order-disorder type. The N-H distance of $1.03 \pm 0.02 \text{ \AA}$ found for both the hydrogen and deuterium compound is closely equal to that found in ND_4Br ,^{4,17} $1.03 \pm 0.02 \text{ \AA}$ by neutron diffraction, and in good agreement with values obtained by nuclear magnetic resonance¹⁸ 1.025 and 1.039 \AA, respectively. The thermal motion of hydrogen as indicated by both B and α appears to be somewhat greater than that of deuterium, in accord with expectation.

Since ND_4Cl patterns at -180°C and -78°C showed no essential differences, the line width transition at about -140°C in NH_4Cl observed in nuclear magnetic resonance experiments¹⁹ may be reasonably presumed to involve no appreciable change in atomic positions.

¹⁷ The smaller value quoted in reference 3 is revised upward when the new value of f_N is used.

¹⁸ Gutowsky, Kistiakowsky, Pake, and Purcell, *J. Chem. Phys.* **17**, 972 (1949).

¹⁹ H. S. Gutowsky and G. E. Pake, *J. Chem. Phys.* **16**, 1164 (1948).

Scattering of Electrons in Metals by Dislocations*

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The problem of the change in electrical conductivity in metals upon cold-working is treated by the method of Koehler in which the scattering of electrons by pairs of parallel edge-type dislocations is assumed to be the major effect. A comparison is made between the electronic shielding assumed in the scattering potential used by Koehler and the shielding assumed by Landauer in a somewhat different treatment. The large effect of the discontinuity in the ionic displacement across the plane connecting the dislocation axes is shown to cancel that of a previously neglected term in the scattering potential. The scattering matrix element is evaluated, and the change in resistivity is computed by the perturbation method of Mackenzie and Sondheimer. Finally, the anisotropy in the resistivity is discussed, and it is shown that the slip direction is the direction of low resistivity.

I. INTRODUCTION

SEVERAL recent publications¹⁻⁴ have treated theoretically the problem of the change in electrical conductivity of metals upon cold-working. In all of this work it is assumed that the change is primarily because of the scattering of electrons from edge-type dislocations, and the possible effects of associated clusters of vacancies, or of screw-type dislocations, are ignored. The calculations differ mainly in the type of

scattering potential employed, Koehler¹ (K) and Mackenzie and Sondheimer² (MS) using in their potentials the ionic displacements around a pair of dislocations, and Landauer³ (L) and Dexter⁴ (D) making use of only the density change. These two potentials take account of the shielding of the positive charge by the electrons in somewhat different ways. In Sec. II a general comparison is made among these methods and Bardeen's self-consistent method⁵; it is shown that all three approaches agree in the limit of slowly varying potentials, i.e., perfect shielding.

One of the characteristic features of an edge-type dislocation is that there is a discontinuity in the ionic displacement across the missing plane of atoms. In the

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¹ J. S. Koehler, *Phys. Rev.* **75**, 106 (1949), to be referred to as K.

² J. K. Mackenzie and E. H. Sondheimer, *Phys. Rev.* **77**, 264 (1950), to be referred to as MS.

³ Rolf Landauer, *Phys. Rev.* **82**, 520 (1951), to be referred to as L.

⁴ D. L. Dexter, *Phys. Rev.* **85**, 936 (1952), to be referred to as D.

⁵ J. Bardeen, *Phys. Rev.* **52**, 688 (1937).