

The rather unreasonable decrease in  $\theta'$  with nickel content predicted by all such exchange calculations strongly suggests the presence of some other mechanism. Large admixtures of  $p$  and  $d$  states to the conduction band with additions of nickel to copper could give rise to an appreciable Van Vleck temperature-independent paramagnetism as discussed by Kubo and Obata,<sup>11</sup> and such admixtures do not seem unreasonable in view of the

<sup>11</sup> R. Kubo and Y. Obata, *J. Phys. Soc. Japan* **11**, 547 (1956).

rapid changes in optical, thermal, electric, and magnetic properties of these alloys as the nickel content is increased.

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## Energy Loss of Fast Charged Particles in LiH

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The quantum theory of the electromagnetic interaction of particles and fields in dense matter predicts that fast charged particles lose their kinetic energy to longitudinal electronic excitations influenced by one-electron and collective effects. Both effects are to be expected in metals and insulators, but to varying degrees. A clear identification of collective excitations in insulators is still lacking.

LiH is the best-suited crystal for predicting the one-electron and collective effects on the longitudinal electronic excitations in an insulator, and for verifying such prediction experimentally. The characteristic energy loss spectrum and the mean excitation potential of the LiH crystal are estimated. One finds that the longitudinal excitations in this insulator crystal are of predominantly collective character. The results are so significantly different from those obtained by neglecting collective effects that stopping experiments in single as well as in multiple scattering can clearly identify the collective effects and confirm the theoretical predictions.

### 1. STATEMENT OF PROBLEM

CHARACTERISTIC energy losses of singly scattered electrons are observed in metals and insulators.<sup>1</sup> The quantum theory of electromagnetic interactions of particles and fields in dense substances attributes these energy losses to the excitation of longitudinal oscillations with both one-electron and collective ("plasma") components.<sup>2,3</sup> However, it has been argued that electrons in filled bands cannot oscillate collectively,<sup>4,5</sup> and that, in any event, characteristic energy losses can be explained entirely by one-electron band transitions.<sup>6-7</sup> A clear-cut experimental identification of collective oscillations in insulators is still lacking and would be desirable.

LiH is the insulator with the fewest electrons per atom and with the highest ratio of valence- to core-electrons, to which Bragg's additivity rule for stopping powers is least applicable. It is best suited for estimating theoretically the one-electron and collective effects on the longitudinal excitations of the valence

electrons, and for giving decisive experimental confirmation of the importance of collective effects in an insulator, as predicted by theory. In the following, the characteristic energy-loss spectrum and the mean excitation potential of the LiH crystal are estimated. One finds that fast charged particles should excite the valence electrons to energy levels of predominantly collective character. The results differ so significantly from those one obtains by considering only one-electron band transitions (which is not justified by theory) that stopping experiments in single scattering and multiple scattering can demonstrate clearly the excitation of collective polarization oscillations in this insulator crystal.

### 2. EXCITATION LEVELS

Suppose the response of a substance to an electrodynamic disturbance can be described by the excitation of coupled one-electron and field oscillators. One may then separate these oscillators into their transverse and longitudinal normal modes by a suitable transformation of the total Hamiltonian.<sup>3</sup> The transverse normal modes do not contain collective components. They correspond to just the one-electron oscillators ( $f_n, \omega_n$ ) of oscillator strength  $f_n$  and frequency  $\omega_n$  in the semiempirical Drude-formulation of the dielectric constant  $\epsilon(\omega)$ . The eigenfrequencies of the longitudinal normal modes are given by the solutions  $\omega = \Omega_n$  of the equation  $\epsilon(\omega) = 0$ .

<sup>1</sup> L. Marton, *Revs. Modern Phys.* **28**, 172 (1956).

<sup>2</sup> D. Pines, *Revs. Modern Phys.* **28**, 184 (1956).

<sup>3</sup> U. Fano, *Phys. Rev.* **103**, 1202 (1956).

<sup>4</sup> P. A. Wolff, *Phys. Rev.* **92**, 18 (1953); however, see H. Kanazawa, *Progr. Theoret. Phys. Japan* **13**, 227 (1955).

<sup>5</sup> R. H. Tredgold, *Physica* **22**, 1219 (1956).

<sup>6</sup> Leder, Mendlowitz, and Marton, *Phys. Rev.* **101**, 1460 (1956).

<sup>7</sup> E. J. Sternglass, *Nature* **178**, 1387 (1956).

They define a set of coupled oscillators ( $F_{n'}, \Omega_{n'}$ ), where

$$F_{n'} = \{\omega_p^2 [d\epsilon(\omega)/d(\omega^2)]_{\Omega_{n'}}\}^{-1} \simeq f_n$$

and

$$\Omega_{n'}^2 \simeq \omega_n^2 + \omega_p^2 f_n,$$

as long as the damping is small and the  $\omega_n$  are so widely spaced that  $\omega_p^2 f_n \ll \omega_{n+1}^2 - \omega_n^2$ . The frequency  $\omega_p = (4\pi e^2 \rho / m)^{1/2}$  is the "plasma" frequency in a substance with an electron density  $\rho$ .

The transverse modes ( $f_n, \omega_n$ ) are observed as optical absorption bands or in anomalous dispersion as the poles of  $\epsilon(\omega)$ ; the longitudinal modes ( $F_{n'}, \Omega_{n'}$ ) are observed in the stopping of charged particles or (as in the case of alkali metals) as the limiting frequencies for metallic reflection.

### 3. CHARACTERISTIC ENERGY LOSSES

The characteristic energy losses of singly scattered electrons correspond to the excitation of the longitudinal oscillators ( $F_{n'}, \Omega_{n'}$ ). Generally, one finds for inner atomic shells that  $\hbar\Omega_i \simeq \hbar\omega_i \gtrsim \hbar\omega_p f_i^{1/2}$ , i.e., the one-particle behavior predominates. This applies also to most molecular substances, where the mean density of valence electrons is so low that  $\hbar\Omega_{\text{val}} \simeq \hbar\omega_{\text{val}} > \hbar\omega_p f_{\text{val}}^{1/2}$ . In metals with tightly bound ion-core electrons, one finds  $\hbar\omega_i \gg \hbar\Omega_{\text{val}} \simeq \hbar\omega_p f_{\text{val}}^{1/2} > \hbar\omega_{\text{val}}$ . In ionic and valence lattices, and in transition and noble metals, the situation varies between these two extremes.<sup>8</sup> Corrections for damping, ion-core polarization, and local-field effects are negligibly small if  $\hbar\omega_p f_{\text{val}}^{1/2} > \hbar\omega_{\text{val}}$ , i.e., if collective oscillations are the determining mode in the longitudinal excitation of valence electrons. This should be the case in the LiH crystal.

### 4. MEAN EXCITATION POTENTIAL

In the theory of the stopping power of matter for fast charged particles, the only characteristic material constant is the mean excitation potential  $I$  of the stopping electrons in the target material. It is averaged according to

$$\ln I = \sum_n F_n \ln \hbar\Omega_n, \quad (1)$$

over all excitation levels ( $F_n, \Omega_n$ ). Equation (1) gives the exact prescription for obtaining the  $I$  value of any substance, which, however, in practice can be applied only to the lightest elements. For complicated systems, semiempirical approximation methods must be used. Depending on the approximations made for the solutions of the equation  $\epsilon(\omega) = 0$ , they fall into two groups. They will be referred to as the *optical* and *statistical method*.

#### a. Optical Method

In the optical method one sets  $F_n = f_n$  and  $\Omega_n = \omega_n$ , i.e., one neglects the collective components, so that optical absorption data can be used for estimating mean excitation potentials. The resulting  $(I_n)_{\text{opt}}$  values

<sup>8</sup> W. Brandt, Phys. Rev. **104**, 691 (1956); **105**, 734(E) (1957).

are then lower limits. In this approximation, the optical method is limited to cases where not only

$$\eta_n^2 \equiv (1 + \omega_p^2 f_n / \omega_n^2) \ll \omega_{n+1}^2 / \omega_n^2$$

(see Sec. 2), but specifically  $\eta_n^2 \simeq 1$ . However, if  $1 < \eta_n^2 \ll \omega_{n+1}^2 / \omega_n^2$ , the frequency becomes  $\Omega_n^2 = \eta_n^2 \omega_n^2$ . Inserting this expression in Eq. (1) and approximating  $f_n$  by the relative occupation number  $N_n N^{-1}$  yields

$$\ln I = N^{-1} \sum_n N_n \ln [\eta_n (I_n)_{\text{opt}}] = \ln [\bar{\eta} I_{\text{opt}}]. \quad (2)$$

Detailed estimates of  $\bar{\eta}$  ("zero-energy" polarization effect)<sup>8,9</sup> show that indeed  $\bar{\eta} \lesssim 1.1$  for most substances.

#### b. Statistical Method

A second method with emphasis on the collective behavior of electrons can be derived from the statistical model of the atom. In this model, the relative contributions of both the one-electron and the collective modes of oscillation to the dynamic behavior of the electron cloud are prescribed by the electron density distribution; they vary continuously with the distance  $\mathbf{r}$  from the nucleus, but are nearly independent of the atomic number  $Z$ .

Taking the collective component to be the indicative term for the dynamic behavior, one may approximate Eq. (1) by Eq. (3):

$$\ln I = N^{-1} \int \rho(\mathbf{r}) d^3r \ln [\chi(\mathbf{r}) \hbar\omega_p(\mathbf{r})], \quad (3)$$

where  $N = \int \rho(\mathbf{r}) d^3r$  and  $\omega_p(\mathbf{r}) = [4\pi e^2 \rho(\mathbf{r}) / m]^{1/2}$ . The function  $\chi(\mathbf{r}) = [1 + \omega_0^2(\mathbf{r}) / \omega_p^2(\mathbf{r})]^{1/2}$  measures the relative contributions of the collective and one-electron frequency components. On an atomic scale, Eq. (3) is analogous to Eq. (1) in that it averages over the continuous frequency spectrum of the statistical atom. It should be a good approximation, because the main contributions come from the bulk of the electron cloud to which the statistical model applies best. Equation (3) includes the contributions of the long-range collective oscillations in dense substances as density-dependent changes of  $\rho(\mathbf{r})$ , and the accompanying changes of  $\chi(\mathbf{r})$ . In fact, if the atomic interaction is sufficiently strong, or, equivalently, if the density of a substance is sufficiently high,  $\rho(\mathbf{r})$  varies only slowly throughout the substance. Then,  $I(\mathbf{r}) = \chi(\mathbf{r}) \hbar\omega_p(\mathbf{r})$  can be considered as the average pertinent to  $\mathbf{r}$  over momentum space, as defined by Eq. (1) including the long-range collective effects, and Eq. (3) as a Stieltje-integral (relative to a local Debye length) over space coordinates, to complete the averaging over phase space. Equation (3) will be applied in this sense to the valence electrons of the LiH crystal. Lindhard and Scharff<sup>10</sup> first discussed Eq. (3) and tested its applicability to light elements.

<sup>9</sup> R. M. Sternheimer, Phys. Rev. **92**, 351 (1954).

<sup>10</sup> J. Lindhard and M. Scharff, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. **27**, No. 15 (1953).

If  $\omega_0=0$  and  $\rho=\text{constant}$ , Eq. (3) yields Kramers' mean excitation potential of an isotropic electron plasma.

The electron density distribution of the Thomas-Fermi model is not a good approximation for light elements. If one approximates  $\rho(\mathbf{r})$  by hydrogenic wave functions, Eq. (3) breaks up into shell contributions. For example, one finds by inserting in Eq. (3) Slater wave functions of effective quantum number  $n^*$  and effective charge  $Z_n^*$  that

$$(I_n)_{\text{stat}} = 2^{\frac{3}{2}} \frac{N_n^{\frac{1}{2}}}{\Gamma^{\frac{1}{2}}(2n^*+1)} \left( \frac{Z_n^*}{n^*} \right)^{\frac{3}{2}} \text{ry} \exp\left[ (n^*-1)F(2n^*+1) - (n^*+\frac{1}{2}) \right], \quad (4)$$

where  $F(y) = d \ln \Gamma(y) / dy$ . In this case,

$$\ln I = N^{-1} \sum_n N_n \ln [\chi_n (I_n)_{\text{stat}}] = \ln [\bar{\chi} I_{\text{stat}}], \quad (5)$$

in analogy to Eq. (2). In particular, for  $K$  shells,

$$(I_1)_{\text{stat}} = 0.893 N_1^{\frac{1}{2}} Z_1^{*\frac{3}{2}} \text{ry}, \quad (6)$$

and, for  $L$  shells,

$$(I_2)_{\text{stat}} = 0.151 N_2^{\frac{1}{2}} Z_2^{*\frac{3}{2}} \text{ry}. \quad (7)$$

If applied to dense substances, the validity ranges of the two methods can be assessed roughly by considering the relation  $(\eta_n^2-1)(\chi_n^2-1)=1$ . If  $\eta_n^2 < 2$ , the optical method offers the better approximation; if  $\chi_n^2 < 2$ , the statistical method. If  $\eta_n^2 \simeq \chi_n^2 \simeq 2$ , both methods should be equivalent but least accurate. For the conduction electrons of most metals,  $\chi_{\text{val}}^2 \simeq 1$  and, hence,  $I_{\text{val}} = \hbar \omega_p f_{\text{val}}^{\frac{1}{2}}$ .

It is important to note that Eq. (3) has been obtained by an essentially heuristic argument from the assumptions that the atomic frequency distribution is described correctly by  $\rho(\mathbf{r})$ , and that  $\rho(\mathbf{r})$  varies slowly in space compared to the local interelectronic spacing. Both assumptions are open to question in many instances.  $I$  values depend primarily on a sum rule and are in most cases insensitive to the details of the energy transfer mechanism. The sum rule is evidently well approximated by Eq. (3) because the  $I_{\text{stat}}$  values of atoms in all tested cases, including those pertaining to Eqs. (5)–(7), are found to agree (within the uncertainty of  $\bar{\chi}$ ) with  $I$  values obtained by Eq. (2)<sup>11</sup> and by experiment. Such agreement is also found for the more general results derived in the appendix from the statistical model of the atom.

The situation is different for the LiH crystal. Its  $I$  value is indeed sensitive to the excitation mechanism, because the summation extends over excitation levels of only a few electrons per atom, of which one-half are valence electrons. Nevertheless, one is justified in applying Eq. (3) to LiH, because the valence electron density is so high that  $\chi_{\text{val}} \sim 1$ , and varies sufficiently slowly. Characteristic energy loss spectra, of course,

<sup>11</sup> W. Brandt, *Health Physics* **1**, 11 (1958).

are inherently sensitive to the excitation mechanism. Therefore, the longitudinal excitation levels of the valence electrons in LiH can be identified by measurements of either  $I$  or the characteristic energy loss spectrum of charged particles, and the theoretical estimates of Sec. 5 confirmed accurately.

## 5. APPLICATION TO LiH

A mixture of isolated atoms obeys Bragg's additivity rule for stopping powers; that is, the stopping power of such a "Bragg-gas" is equal to the stoichiometric sum of the stopping powers of the component atoms.<sup>11</sup> Let a Bragg-gas be composed of Li and H atoms and ions such that its charge distribution corresponds to the mean charge distribution in the LiH crystal. For brevity, one may write  $\text{Li}^{+a}\text{H}^{-a}$ ;  $a=0$  denotes covalent bonding,  $a=1$  ionic bonding. The mean excitation potential of the Bragg-gas is then

$$I_0(\text{Li}^{+a}\text{H}^{-a}) = [I_0^2(\text{Li}^+)I_0^2(\text{H}^-)]^{a/4} [I_0^3(\text{Li})I_0(\text{H})]^{(1-a)/4}.$$

The subscript 0 denotes isolated atoms. With the  $I_0$  values of the various atomic species, obtained as described in Sec. 4, one finds  $11 \leq I_0(\text{LiH}) \leq 26$  (ev) for  $1 \geq a \geq 0$ . The electron density distribution calculated by Mueller and Eyring<sup>12</sup> for the LiH molecule corresponds to  $a=0.55$ , for which case  $I_0(a=0.55)=19$  ev. As for Be,<sup>13</sup> Bragg's rule is quite inadequate for LiH, because 50% of the stopping electrons reside in valence shells; inserting the actual electron density distribution in Eq. (3) yields twice the  $I_0$  value, namely  $I_{\text{mol}}=38$  ev.

The statistical method can be applied to the valence electrons in the LiH crystal, because  $\hbar \omega_p f_{\text{val}}^{\frac{1}{2}} = 13$  ev, whereas the optical absorption edge lies near 7 ev,<sup>14,15</sup> i.e.,  $\chi_{\text{val}}^2 < 2$ . In the following,  $\bar{\chi}$  is set tentatively equal to unity. The electron density distribution has been calculated by Ewing and Seitz<sup>15</sup> from approximate solutions of the Hartree-Fock equations of the crystal, and by Lundquist<sup>16</sup> by the molecular orbital method. They agree quite closely with one another and correspond to the gross charge distribution  $a=0.3$ . The experimental density distribution<sup>17</sup> corresponds to  $a=0.46$  and deviates in details from the theoretical distributions. For the latter, one obtains by Eq. (3)  $I(0.3)=39$  ev,<sup>18</sup> for the former  $I(0.46)=41$  ev. A lower limit for  $I$  is obtained by assuming the valence electrons to be free, i.e.,  $I(a) \gtrsim I(f) = I^{\frac{1}{2}}(\text{Li}^+) (\hbar \omega_p f_{\text{val}}^{\frac{1}{2}})^{\frac{1}{2}} = 31$  ev.  $I(f)$  would correspond to the mean excitation potential of a covalent lattice,  $I(0)$ . The valence electrons in a purely ionic lattice would have a He-like configuration in the H cell. The physical conditions in this hypothetical lattice actually exceed the validity range of

<sup>12</sup> C. R. Mueller and H. Eyring, *J. Chem. Phys.* **19**, 934 (1951).

<sup>13</sup> A. Bohr, *Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd.* **24**, No. 19 (1948).

<sup>14</sup> W. Rausch, *Z. Physik* **111**, 650 (1939).

<sup>15</sup> D. W. Ewing and F. Seitz, *Phys. Rev.* **50**, 760 (1936).

<sup>16</sup> S. O. Lundquist, *Arkiv Fysik* **8**, 177 (1954).

<sup>17</sup> W. Cochran, *Revs. Modern Phys.* **30**, 47 (1958).

<sup>18</sup> W. Brandt, *Physik. Verhandl.* **8**, 188 (1957).

Eq. (3). Formal application of Eq. (3) gives an upper limit for  $I(1)$  reflecting the excitation levels of highly compressed  $H^-$  ions. One finds  $I(1) < 54$  ev. If charged particles were not to excite collective oscillations in the LiH crystal, the 7-ev band transition should be the determining excitation, and  $I = 23$  ev. These results are summarized in Fig. 1. The corresponding stopping powers differ sufficiently for an experimental confirmation of the preponderance of collective over one-electron excitations.\*

The following characteristic energy-loss spectrum is to be expected for the LiH crystal. If only band transitions were excited (corresponding to  $I = 23$  ev), the predominant energy loss would appear as a broad peak near 7 ev. Higher losses have lower intensity. If, as expected theoretically, collective oscillations are excited also (corresponding to  $I = 39$  ev), a pronounced peak appears at  $\chi_{val} \hbar \omega_p f_{val}^{\frac{1}{2}} = 14.5$  ev, for  $\chi_{val} = 1.14$ . In addition, multiples of the 14.5-ev peak occur with decreasing intensity, and possibly weak combinations of the one-electron and collective loss peaks. The excitation of the Li  $K$  shell should not contribute to energy losses  $< 70$  ev.

The approximate nature of the methods of calculation, and particularly Eq. (3), makes it difficult to assess the accuracy of the numerical estimates of  $I$  and the characteristic energy-loss spectrum. Judging from experience with other light substances, the error in the numerical results should not exceed significantly the uncertainty in the proper choice of  $\bar{\chi}$ . The  $I$  values of LiH are given for  $\bar{\chi} = 1$ . A more detailed estimate shows that  $1 \leq \bar{\chi} \leq 1.25$ ; in fact,  $\bar{\chi} = 1.1$  is consistent with the expected characteristic energy loss 14.5 ev. In other words, the theoretical estimates of the mean excitation potential and main characteristic energy loss in crystalline LiH, if taken separately, have an uncertainty of *ca.* 20%. Both combined must be consistent with one another, which reduces the uncertainty to *ca.* 10%.

\* Note added in proof.—R. L. Platzman [*Symposium on Radiobiology*, edited by J. J. Nickson (John Wiley and Sons, Inc., New York, 1952), p. 160] has remarked that the stopping power of a substance composed alternately of  $H^+$  and  $H^-$  atoms would exceed the stopping power of  $H_2$  by *ca.* 50%. It should be noted that this statement actually refers to the stopping power of the ionic Bragg-gas as compared to the stopping power of gaseous  $H_2$ . Even if the one-electron excitation levels of  $H^-$  in condensed  $H^+H^-$  were not significantly different from the one-electron excitation level of free  $H^-$  (as Platzman implicitly assumes), collective effects would reduce this difference at the densities of liquid (boiling)  $H_2$  (0.07 g/cm<sup>3</sup>) and of solid  $H_2$  (0.09 g/cm<sup>3</sup>). One can demonstrate this change by estimating the respective mean excitation potentials of  $H^+aH^-a$  for  $a=0$  and  $a=1$ . Using the methods and notation of the present paper, one finds that  $I_0(0) = 15$  ev and  $I_0(1) = 0.8$  ev, whereas for gaseous  $H_2$   $I_{mole} = 18$  ev. For the liquid phase, one estimates  $I_l(0) = 19.5$  ev and  $I_l(1) = 7.6$  ev, for the solid phase  $I_s(0) = 20$  ev and  $I_s(1) = 8.6$  ev. The relative differences of the covalent and ionic mean excitation potentials,  $[I(0) - I(1)]/I(0)$ , decrease from 1 to 0.6 in condensing hydrogen from the gas phase into the liquid and solid phases. The condensation of  $H_2$  entails an increase of the mean excitation potential by 10%. The  $I_{mole}(0)$ ,  $I_l(0)$ , and  $I_s(0)$  should nearly coincide numerically with the main characteristic energy-loss lines of the three phases of  $H_2$ .

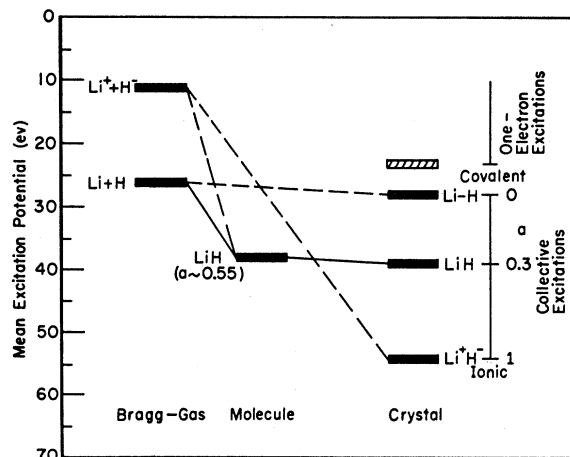


FIG. 1. Mean excitation potentials of LiH in different valence states. The solid line connects the theoretically expected  $I$  values.

An angle dependence of characteristic energy losses *per se* cannot give information about the collective nature of energy losses. The magnitude of the angle dependence in insulators depends so sensitively on the details of the electronic structure that accurate predictions would have to be based on a self-consistent field calculation of the LiH crystal. Such a calculation is desirable also in view of the discrepancies between the presently available theoretical and experimental electron density distributions. Nevertheless, one can estimate that the dispersion coefficient<sup>19,20</sup> for the characteristic energy loss in LiH is approximately equal to  $0.51\chi_{val}^2 \approx 0.7$ , where 0.51 is taken to be the dispersion coefficient for the case  $\chi_{val} = 1$ .

## 6. SUMMARY

The main purpose of this paper is to draw attention to crystalline LiH as the best-suited substance for a comprehensive theoretical and experimental investigation of longitudinal electronic excitations in insulators. Estimates of the characteristic energy-loss spectrum and the mean excitation potential of LiH are given. It is shown that stopping experiments under conditions of single and of multiple scattering can clearly identify the excitation of collective oscillations in this insulator crystal. The combined measurements of both experiments can provide sensitive tests of the theory of longitudinal excitations in insulators for LiH, because the results of both must be quantitatively consistent with the same electronic excitation levels.

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<sup>19</sup> R. A. Ferrell, *Phys. Rev.* **107**, 450 (1957).

<sup>20</sup> H. Kanazawa and S. Tani, *Progr. Theoret. Phys. (Japan)* **19**, 153 (1958).

## APPENDIX

Lindhard and Scharff applied Eq. (3) to the statistical Thomas-Fermi (TF) model of the atom. This leads directly to Bloch's relation  $I=KZ$ . It is of interest to consider  $I(Z)$  for the Thomas-Fermi-Dirac (TFD) model, which includes the exchange interaction between electrons.<sup>8</sup> However, the TFD density distribution is not an explicit function of  $Z$  and hence not suited for the present purpose. A sufficiently accurate approximation is the TFX distribution, which follows from the TF distribution by a simple coordinate contraction  $r_{\text{TFX}}=\lambda^{-1}r_{\text{TF}}$ . The scaling parameter  $\lambda$  can be determined by the variational condition

$$\frac{\partial E}{\partial \lambda} = -[\lambda^2 E_{\text{kin}} + \lambda(E_{\text{pot}} + E_{\text{exch}})] = 0.$$

Introducing the proper expressions<sup>21</sup> for the  $E$  in terms of the solution  $\varphi_0$  of the TF equation  $\varphi_0'' = \varphi_0^3 x^{-3/2}$ , with  $x = \mu^{-1}r$ , one finds

$$\lambda_0 = 1 + \left(\frac{\pi}{2}\right)^{1/2} \frac{\kappa_a'}{\kappa_b} \frac{\mu}{Z^{1/2}} \int_0^\infty \varphi_0^2 dx / \int_0^\infty \varphi_0^3 x^{-3/2} dx = 1 + 0.16Z^{-1/2}.$$

The coefficient 0.16 is a lower limit for the  $Z^{-1/2}$  de-

<sup>21</sup> P. Gombás, *Die statistische Theorie des Atoms und ihre Anwendungen* (Springer-Verlag, Wien, 1949). See pp. 390-392.

pendence of  $\lambda$ . Inserting  $\rho_{\text{TFX}} = (Z\lambda_0^3/4\pi\mu^3)(\varphi_0/x)^3$  in Eq. (3) yields

$$I_0 = 0.451\bar{\chi}_0\lambda_0^3 Z \text{ ry.}$$

For the evaluation of the constant  $\bar{\chi}_0$ , one may use the fact that in the statistical model  $\omega_0$  and  $\omega_p$  depend linearly on  $Z$ . If

$$\omega_0^2 = -(e/mr)(dP/dr)$$

with

$$P = (Ze/r) - (1-1/Z) \int_0^\infty e\rho_{\text{TF}}(\xi) |\xi-r|^{-1} d^3\xi,$$

one finds for  $Z \gg 1$  and with the abbreviation

$$q_0 = \varphi_0 - x\varphi_0',$$

that

$$\ln \bar{\chi}_0 \simeq \frac{1}{2} \int_0^\infty \varphi_0^3 x^3 dx \ln(1+q_0/x^3 \varphi_0^3) = \ln 1.78.$$

Hence,

$$I_0 = 0.802\lambda_0^3 Z \text{ ry} \simeq 10.9(1+0.25Z^{-1/2})Z \text{ (ev)}.$$

In essence, this result confirms an earlier estimate by Jensen<sup>22</sup> for a highly simplified atomic model, and agrees with experimental observations.<sup>8,23</sup> It approaches Bloch's relation for large  $Z$ .

<sup>22</sup> H. Jensen, *Z. Physik* **106**, 620 (1937).

<sup>23</sup> W. Brandt (to be published).

Crystal Structure and Ferrimagnetism in NiMnO<sub>3</sub> and CoMnO<sub>3</sub>

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X-ray diffraction studies of individual crystals of NiMnO<sub>3</sub> and CoMnO<sub>3</sub> show that these compounds have the structure of ilmenite (space group  $R\bar{3}$ ). The crystals have a plate-like crystal habit with the threefold symmetry axis perpendicular to the faces of the platelet. Positions of atoms within the unit cell have been determined by comparing calculated structure factors with those obtained from x-ray powder patterns. There are two Ni-O-Mn configurations that appear to be favorable to a magnetic superexchange interaction, and these are sufficient to extend magnetic ordering in three dimensions.

## I. INTRODUCTION

**SUPEREXCHANGE** interactions in rhombohedral sesquioxides with particular reference to Cr<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and their solid solutions have been discussed by Li.<sup>1</sup> The discussion can now be extended to include ferrimagnetism in the compounds NiMnO<sub>3</sub> and CoMnO<sub>3</sub> which have the same structure as the mineral ilmenite (FeTiO<sub>3</sub>).<sup>2-4</sup> This  $ABX_3$  structure is related

<sup>1</sup> Y. Y. Li, *Phys. Rev.* **102**, 1015 (1956).

<sup>2</sup> The synthesis and bulk magnetic properties of these compounds have been discussed by Swoboda, Vaughan, and Toole<sup>3</sup> and Bozorth and Walsh.<sup>4</sup>

<sup>3</sup> Swoboda, Vaughan, and Toole, *J. Phys. Chem. Solids* (to be published).

<sup>4</sup> R. M. Bozorth and D. E. Walsh, *J. Phys. Chem. Solids* (to be published).

to that of Cr<sub>2</sub>O<sub>3</sub>, where both  $A$  and  $B$  are Cr atoms. The metal atoms of ilmenites are arranged in alternate layers between oxygen layers and are ordered in the sequence  $AB-BA-AB-BA$  along the body diagonal of the rhombohedron.

The principal geometric parameters for qualitative understanding of superexchange interactions are the metal-to-oxygen distances and the metal-oxygen-metal angles. In order to consider such interactions in NiMnO<sub>3</sub> and CoMnO<sub>3</sub>, the exact positions of the individual atoms must be determined. Proof of ordering of the metals into the  $AB-BA-AB$  sequence was obtained from x-ray diffraction studies of individual crystals. Positions of atoms within the unit cell were determined