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Excitation of Molecular Rotation-Vibration by Electron Impact

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The integral equation for the scattering of an electron from a symmetric diatomic molecule is solved approximately to obtain the effective interaction integral between the electron and the molecular vibration-rotation, neglecting polarization and exchange. This interaction depends on the difference of phase of the incident wave function between the two nuclear centers and thus on the momentary direction and magnitude of the internuclear radius vector. From this interaction function the effective cross sections for rotation-vibration excitation are computed and, by various sum rules, a closed formula for mean loss of energy of the electron to molecular rotation-vibration is obtained. This is compared with the corresponding loss of energy of the rebounding electron to the motion of the center of gravity of the molecule. These two quantities are shown to be the same order of magnitude, their ratio changing from $\frac{1}{3}$, for very small equilibrium internuclear distance, to 1, for very large internuclear distance.

I. INTRODUCTION

THE scattering of an electron from a potential field $V(r)$ is described by a solution of the integral equation,[1]

$$\psi(\mathbf{r})=e^{i\mathbf{k}_i\cdot\mathbf{r}}-\frac{2m}{\hbar^2}\int\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{4\pi|\mathbf{r}-\mathbf{r}'|}V(\mathbf{r}')\psi(\mathbf{r}')dv', \quad (1)$$

where $k=(mv/\hbar)$, v being the incident electronic speed, where $\mathbf{k}_i=k\mathbf{a}_i$, $\mathbf{a}_i$ being a unit vector in the incident direction, and where $\mathbf{r}$ is the radius vector giving the position of the electron. To obtain the scattered wave we obtain the asymptotic form[2] for,

$$\begin{aligned}&\psi(\mathbf{r})\to e^{i\mathbf{k}_i\cdot\mathbf{r}}+(e^{ikr}/r)f(\vartheta),\\ &f(\vartheta)=-\frac{m}{2\pi\hbar^2}\int e^{-i\mathbf{k}_s\cdot\mathbf{r}'}V(\mathbf{r}')\psi(\mathbf{r}')dv',\end{aligned} \quad (2)$$

where $f(\vartheta)$ is the angle-distribution factor for the scattered wave, from which we obtain the cross section for scattering; $\mathbf{k}_s=k\mathbf{a}_s$, where $\mathbf{a}_s$ is a unit vector in the direction of the scattered electron. If ψ is known exactly Eq. (2) is an exact expression and $|f|^2$ will produce exact expressions for the differential and total cross sections for elastic scattering from the potential V.

If now the potential field of a symmetric diatomic molecule may be broken into two equal parts, each centered about a nucleus,

$$V(\mathbf{r})\simeq U(\mathbf{r}-\tfrac{1}{2}\mathbf{R})+U(\mathbf{r}+\tfrac{1}{2}\mathbf{R}), \quad (3)$$

where $\mathbf{R}$ is the internuclear radius vector, then, to the approximation for which this separation is valid, Eq. (2) may be further simplified. For example, we may show that, to a fairly good approximation, the two integrals about the two nuclei differ only by a phase factor, and that

$$f(\vartheta)\simeq 2f_a(\vartheta)\cos[\tfrac{1}{2}(\mathbf{k}_i-\mathbf{k}_s)\cdot\mathbf{R}], \quad (4)$$

where

$$\begin{aligned}f_a(\vartheta)&\simeq e^{-\frac{1}{2}\mathbf{k}_i\cdot\mathbf{R}}\left(\frac{m}{2\pi\hbar^2}\right)\int e^{-i\mathbf{k}_s\cdot\mathbf{r}'}U(\mathbf{r}')\psi(\mathbf{r}'+\tfrac{1}{2}\mathbf{R})dv'\\ &\simeq e^{\frac{1}{2}i\mathbf{k}_i\cdot\mathbf{R}}\left(\frac{m}{2\pi\hbar^2}\right)\int e^{-i\mathbf{k}_s\cdot\mathbf{r}'}U(\mathbf{r}')\psi(\mathbf{r}'-\tfrac{1}{2}\mathbf{R})dv'.\end{aligned}$$

It may be shown[3] that Eq. (4) is a good approximation even when the Born approximation ($\psi\simeq e^{i\mathbf{k}_i\cdot\mathbf{r}}$) is not valid, and that, when an appropriate $f_a(\vartheta)$ is used, it appears to correspond fairly satisfactorily with experimental results. It is, of course, completely analogous to the formulas for x-ray scattering.

II. INTERACTION WITH EXCITATION-ROTATION

The foregoing is, of course, well-known and is included here only for reference and comparison with the following. Its chief defect is the fact that the molecule is not simply a potential field but is a system which may absorb energy from the incident electron. To take this into account we express the wave function for the N molecular electrons plus the two nuclei as

$$\psi_{\nu,n}=u_\nu(\mathbf{r}_1,\cdots,\mathbf{r}_N)\chi_n(\mathbf{R}), \quad (5)$$

where u_ν is the electronic factor, referred to the nuclei as momentarily fixed and χ is the nuclear part, referred to the molecular center of mass; ν is the electronic quantum numbers, and $n=(n,l,m)$ are the quantum numbers for nuclear motion. This function is a solution of $H_m\psi=E_{\nu,n}\psi$, where H_m is the energy operator for the target molecule.

The equation for the molecule plus incident electron is

$$\left[H_m-\frac{\hbar^2}{2m}\nabla^2+V_m(\mathbf{r},\mathbf{r}_1,\cdots,\mathbf{r}_N,\mathbf{R})\right]\Psi=\left(E_{0,0}-\frac{\hbar^2k_0^2}{2m}\right)\Psi, \quad (6)$$

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[1] N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Clarendon Press, Oxford, 1949), second edition, p. 116.

[2] See reference 1, Chap. II.

[3] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, London, 1952), Chap. IV.

where $E_{0,0}$ is the energy for the initial state, k_0 is $\hbar$ times the initial momentum of the incident electron, $\mathbf{r}$ is the incident electronic position and where V_m is the interaction potential between the incident electron and each electron and nucleus of the molecule. This is equivalent to the integral equation,

$$\begin{aligned}\Psi(\mathbf{r}, \mathbf{r}_1, \cdots, \mathbf{r}_N, \mathbf{R}) \\ =\psi_0 e^{i\mathbf{k}_0\cdot\mathbf{r}}-\frac{2m}{\hbar^2}\sum_{\nu,n}\psi_{\nu,n}\int\cdots\int\frac{\exp(ik_{\nu,n}|\mathbf{r}-\mathbf{r}'|)}{4\pi|\mathbf{r}-\mathbf{r}'|} \\ \times\bar{\psi}_{\nu,n}V_m(\mathbf{r}', \cdots, \mathbf{R}') \\ \cdot\Psi(\mathbf{r}', \mathbf{r}_1', \cdots, \mathbf{r}_N', \mathbf{R}')dv'dv_1'\cdots dv_N'dV', \quad (7)\end{aligned}$$

where dV is the volume element $R^2dR\sin\alpha d\alpha d\beta$ for the internuclear coordinates with respect to the center of mass of the molecule.

If we neglect polarization and exchange effects, the larger part of Ψ, which corresponds to no excitation of the molecule, will have the form $\psi(\mathbf{r})u_0\chi_0$, where ψ is a solution of an equation like (1) and $u_0\chi_0$ is the ground-state wave function for the molecule as defined in Eq. (5). Neglecting cross terms in the sum above, we obtain for the asymptotic form for the part of Ψ corresponding to no electronic excitation,

$$\psi_0 e^{i\mathbf{k}_0\cdot\mathbf{r}}+\textstyle\sum_n u_0\chi_n f_n(\vartheta)\exp(ik_n r)/r$$

$$f_n(\vartheta)\simeq\frac{m}{2\pi\hbar^2}\int dV'\bar{\chi}_n\chi_0\bigg[\int\cdots\int|u_0|^2 \times V_m e^{-i\mathbf{k}_n\cdot\mathbf{r}}\psi(\mathbf{r}')dv'\cdots dv_N'\bigg]. \quad (8)$$

The integral in square brackets in the expression for f_n is quite analogous to that in Eq. (2). The integration over the molecular electronic coordinates produces the average potential of the incident electron with respect to the molecule in the ground state electronically, when the internuclear radius vector is $\mathbf{R}'$.

This average potential can be approximately split into two parts, each centered around one nucleus, as in Eq. (3):

$$\int\cdots\int V_m|u_0|^2dv_1'\cdots dv_N'\simeq U(\mathbf{r}-\tfrac{1}{2}\mathbf{R})+U(\mathbf{r}+\tfrac{1}{2}\mathbf{R}),$$

where the form of $U(\mathbf{r})$ is more or less independent of $\mathbf{R}$. Consequently the whole integral in the brackets in the expression for $f_n(\vartheta)$ is, approximately [see discussion of Eq. (4)],

$$2f_a(\vartheta)\cos[\tfrac{1}{2}(\mathbf{k}_0-\mathbf{k}_n)\cdot\mathbf{R}'],$$

where f_a is an angle-distribution factor approximately equal to that for one of the constituent atoms of the molecule, $\mathbf{k}_0$ is a vector of magnitude $(mv/\hbar)$ directed along the z axis (incident beam), and $\mathbf{k}_n$ is a vector representing the scattered beam, at polar angles ϑ, φ with respect to the z axis, of magnitude k_n such that

$$k_n^2=k_0^2-(2m/\hbar^2)(E_{0,0}-E_{0,n}). \quad (9)$$

The internuclear vector $\mathbf{R}'$ has magnitude R' and polar angles α and β.

We may consequently write the angle-distribution factor $f_n(\vartheta)$, giving the amplitude of the beam scattered after exciting the vibration-rotation states of the molecule from the lowest state ($n=0$) to that represented by quantum number n with no corresponding electronic excitation, as

$$f_n(\vartheta)\simeq 2f_a(\vartheta)\int\cos(\tfrac{1}{2}\boldsymbol{\mu}_n\cdot\mathbf{R}')\bar{\chi}_n(\mathbf{R}')\chi_0(\mathbf{R}')dV', \quad (10)$$

where the vector $\boldsymbol{\mu}_n=\mathbf{k}_0-\mathbf{k}_n$ has a magnitude approximately equal to $(2mv/\hbar)\sin(\frac{1}{2}\vartheta)$, as long as $(E_{0,0}-E_{0,n})\ll(2mv^2)\sin^2(\frac{1}{2}\vartheta)$. To this approximation, therefore, the interaction between the incoming electron and the vibration-rotation states of the molecule is produced by the phase difference of the incident electronic wave function at the two nuclei, as indicated by the cosine term. If the discussion of Massey and Burhop[3] is valid, then it should be expected that this interaction term would be predominant, and would be larger than any interaction term depending on the polarization of the molecule by the incoming electron.

III. EXCITATION PROBABILITIES

If the classical vibration frequency of the diatomic molecule is ω and if the equilibrium separation between the two nuclei is R_0, the allowed vibration-rotation energies and corresponding internuclear wave functions are, approximately,

$$\begin{aligned}E_{0,n}\simeq\epsilon_{n,l}=E_{0,0}+\hbar\omega n+(\hbar^2/MR_0^2)l(l+1), \\ \chi_n(\mathbf{R})\simeq C_n e^{im\beta}P_l^m(\cos\alpha)\exp(-\tfrac{1}{2}b^2x^2)H_n(bx)/(R_0+x),\end{aligned} \quad (11)$$

where $R=R_0+x$, M is the mass of each nucleus, $b^2=M\omega/2\hbar$, n stands for the trio of integers n, l, m wherever it is not necessary to write out all three, where H_n is the nth Hermite polynomial, and where the normalizing factor C_n is given by

$$C_n^2=\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}\frac{b/\sqrt{\pi}}{n!2^n}.$$

In general, the spacing of the rotational levels, dependent on l, is smaller than the spacing of the vibrational levels, dependent on n (i.e., usually $MR_0^2\omega\gg\hbar$). When this is true $bR_0\gg1$, so that $\lim(R\chi)(R\rightarrow0)$ is a negligibly small quantity.

For ease in computation we can take the polar axis for χ to point along $\boldsymbol{\mu}_n$, thus eliminating the unimportant quantum number m. The probability that the incident electron is scattered into the solid angle $d\Omega$ at an angle ϑ to the incident direction, leaving the molecule with no electronic excitation but in the final rotation-vibration state characterized by the numbers l and n (initially $n=l=0$), is then

$$\sigma_{nl}(\vartheta)d\Omega \simeq (k_{nl}/k_0)\,|f_{nl}(\vartheta)|^2 d\Omega,$$

where

$$|f_{nl}|^2=\left(\frac{2l+1}{\pi n!2^n}\right)|f_a|^2\int_{-\infty}^{\infty}\exp(-b^2u^2)H_n(bu)d(bu)$$
$$\times\int_{-\infty}^{\infty}\exp(-b^2v^2)H_n(bv)d(bv)$$
$$\times\int_{-1}^{1}P_l(y)\cos[\tfrac{1}{2}\mu_n(R_0+u)y]dy$$
$$\times\int_{-1}^{1}P_l(z)\cos[\tfrac{1}{2}\mu_n(R_0+v)z]dz, \quad (12)$$

where we have extended the integration over u and v to $-\infty$, which is allowable as long as $bR_0 \gg 1$ as mentioned above.

The differential cross section σ_{00}, for no excitation (purely elastic) is then

$$\sigma_{00}\simeq|f_a|^2\left[\int_{-1}^{1}\exp(-\mu_0^2y^2/16b^2)\cos(\tfrac{1}{2}\mu_0R_0y)dy\right]^2. \quad (13)$$

The maximum value of μ_0 is $2k_0=(2mv/\hbar)$. Therefore the maximum value of the ratio $(\mu_0/16b^2)$ is $(m/M)\times(\frac{1}{2}mv^2/\hbar\omega)$ and unless the initial kinetic energy of the incident electron is smaller than the spacing between vibrational levels, the exponential factor is practically unity and

$$\sigma_{00}\simeq4|f_a|^2(2/\mu_0R_0)^2\sin^2(\tfrac{1}{2}\mu_0R_0), \quad (14)$$

where $\mu_0=(2mv/\hbar)\sin(\frac{1}{2}\vartheta)$. This is the result we would have obtained if we had averaged the f given in Eq. (4) over all orientations of $\mathbf{R}$ and then squared the result.

If the incident electronic kinetic energy is sufficiently larger than the vibrational spacing, the effect of the rotational energies on the magnitude of μ_n is negligible and we can sum σ_{nl} over l to obtain the total cross section for molecular transition from vibrational state 0 to state n for any possible final rotational state. We use the formula

$$\textstyle\sum_l \frac{1}{2}(2l+1)P_l(y)P_l(z)=\delta(y-z) \quad (15)$$

to enable us to integrate over z in Eq. (12). Moreover we can use the formula

$$e^{ixz}=\exp(-\tfrac{1}{4}x^2)\sum_{n=0}^{\infty}(ix)^nH_n(z)/2^nn! \quad (16)$$

to enable us to expand the cosine factors in Eq. (12) and thence to integrate over u and v, eventually obtaining

$$\sigma_n\simeq(k_n/k_0)\textstyle\sum_l|f_{nl}|^2$$
$$\simeq\frac{k_n|f_a|^2}{k_02^nn!}\int_{-1}^{1}[1\pm\cos(\mu_nR_0z)]$$
$$\times\exp(-\mu_n^2z^2/8b^2)(\mu_nz/2b)^{2n}dz, \quad (17)$$

where the plus sign is used if n is even, the minus sign if n is an odd integer. If $(\mu_n/4b)^2 \ll 1$ these integrals may be easily computed; the one for $n=0$ is much larger than the rest in that case.

Finally, if the kinetic energy of the incoming electron is large enough compared to the vibrational spacing so that $k_n\simeq k_0$ for the first ten or twenty vibrational levels, we can sum σ_n over n to obtain the total probability of scattering at an angle ϑ with any amount of vibration-rotation excited,

$$\sigma_{rv}\simeq\textstyle\sum_n\sigma_n\simeq\sum_n|f_n|^2.$$

Here we can use the formula for Hermite polynomials,

$$\sum_{n=0}^{\infty}(1/\pi^{\frac{1}{2}}2^nn!)\exp[-\tfrac{1}{2}(u^2+v^2)]H_n(u)H_n(v)=\delta(u-v), \quad (18)$$

and sum Eq. (12) over both l and n, obtaining

$$\sigma_{rv}\simeq2|f_a|^2\{1+[\sin(\mu_0R_0)/\mu_0R_0]\}, \quad (19)$$

which is to be compared with Eq. (14). This result is obtained by averaging the square of the f of Eq. (4) over all orientations of R. This does not fall off as rapidly as μR increases (ϑ increases), indicating that the large-deflection scattering is more likely to produce vibration-rotation, which is not surprising.

IV. MEAN LOSS OF ENERGY

Finally, when the incoming electron's kinetic energy is large compared with the rotational level spacing we can compute the mean loss of energy, from the electron which has been deflected by an angle ϑ, to rotation-vibration energy of the molecule. This is, of course, the weighted sum of the various allowed energies, $\sum\sigma_{nl}(\epsilon_{nl}-\epsilon_{00})$, divided by the sum of the probabilities $\sum\sigma_{nl}=\sigma_{rv}$.

The term $(\epsilon_{nl}-\epsilon_{00})$ [see Eq. (11)] has two terms, one dependent on n, the other on l. For the terms involving n in the series we use the sum rule for spherical harmonics, Eq. (15), together with Eqs. (12) and (16),

$$\textstyle\sum_{nl}\hbar\omega n|f_{nl}|^2$$
$$=\hbar\omega|f_a|^2\int_{-1}^{1}\exp[-\mu_0^2z^2/8b^2]$$
$$\cdot\sum_{n=1}^{\infty}\frac{1}{(n-1)!}\left(\frac{\mu_0^2z^2}{8b^2}\right)^n[1+(-1)^n\cos(\mu_0R_0z)]dz$$
$$=2\hbar\omega|f_a|^2\left(\frac{\mu_0^2}{8b^2}\right)\int_0^1z^2\left[1+\exp\left(-\frac{\mu_0^2z^2}{4b^2}\right)\right.$$
$$\left.\times\cos(\mu_0R_0z)\right]dz. \quad (20)$$

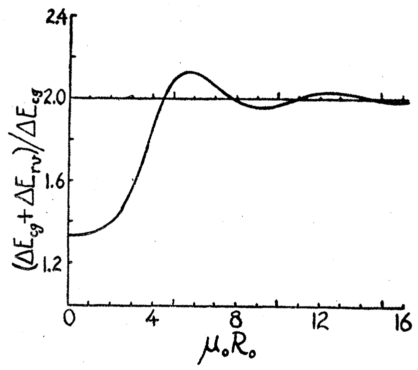

FIG. 1. Ratio between total energy lost to rotation-vibration-translation and energy lost to translation of molecule, as function of $\mu_0R_0=(2mvR_0/\hbar)\sin(\frac{1}{2}\vartheta)$.

For the terms involving l in the series we use Eq. (18) and a modification of Eq. (15) based on the equation for the Legendre polynomials:

$$\int_{-1}^{1}\sum_l \tfrac{1}{2}(2l+1)l(l+1)P_l(z)P_l(z')F(z')dz' =\frac{d}{dz}\left[(1-z^2)\frac{d}{dz}F(z)\right]$$

for any continuous, integrable $F(z)$. The result is

$$\sum_{nl}\left(\frac{\hbar^2}{MR_0^2}\right)l(l+1)|f_{nl}|^2 =\left(\frac{\hbar^2\mu_0^2}{2M}\right)|f_a|^2\int_0^1 \sin^2(\tfrac{1}{2}\mu_0R_0z)(1-z^2)dz \tag{21}$$
$$=\frac{4}{3}|f_a|^2\frac{m}{M}(\tfrac{1}{2}mv^2)(1-\cos\vartheta)[1-j_0(\mu_0R_0)-j_2(\mu_0R_0)],$$

where $j_n(\omega)$ is the spherical Bessel function $(\pi/2\omega)^{\frac{1}{2}}\times J_{n+\frac{1}{2}}(\omega)$ and where $\mu_0=2(mv/\hbar)\sin(\frac{1}{2}\vartheta)$.

When the incident electronic kinetic energy ($\frac{1}{2}mv^2$) is not small compared with the spacing of the vibrational levels [see discussion of Eq. (13)] the exponential in Eq. (20) may be set equal to unity and the sum for the vibrational levels becomes

$$\sum_{nl}\hbar\omega n|f_{nl}|^2\simeq\tfrac{2}{3}|f_a|^2\frac{m}{M}(\tfrac{1}{2}mv^2)(1-\cos\vartheta) \cdot[1+j_0(\mu_0R_0)-2j_2(\mu_0R_0)]. \tag{22}$$

We note that when the equilibrium spacing between molecular nuclei, R_0, is small enough so that $\mu_0R_0\ll1$ then the amount of energy given up by the electron to rotational energy becomes small compared to that donated to vibrational energy, but that when $\mu_0R_0\gg1$ twice as much energy is given up to the rotational motion as to the vibrational. This is to be expected because rotational motion represents two degrees of freedom, vibrational motion only one.

Finally, when the incident electron kinetic energy is large compared to $\hbar\omega$, the average loss of energy to rotation-vibration is the sums of Eqs. (21) and (22) divided by the sum of $|f_{nl}|^2$ given in Eq. (19):

$$(\Delta E)_{rv}\simeq\frac{m}{M}(\tfrac{1}{2}mv^2)(1-\cos\vartheta) \times\left[\frac{1-\frac{1}{3}j_0(\mu_0R_0)-(4/3)j_2(\mu_0R_0)}{1+j_0(\mu_0R_0)}\right]. \tag{23}$$

Classical mechanics indicates that, when $m\ll M$, the energy lost to motion of the center of gravity of a molecule of total mass $2M$, by an electron which is deflected by an angle ϑ by the impact, is

$$(\Delta E)_{cg}\simeq(m/M)(\tfrac{1}{2}mv^2)(1-\cos\vartheta). \tag{24}$$

We therefore see that the total energy lost by the electron to the molecule, when its initial energy is small compared to the molecular electronic excitation energy but large compared to the vibration-rotation energies varies from $(4/3)(\Delta E)_{cg}$ to $2(\Delta E)_{cg}$ as $\mu_0R_0=(2mvR_0/\hbar)\times\sin(\frac{1}{2}\vartheta)$ goes from zero to values much larger than unity. The limiting factor 2 corresponds to the energy the electron would lose if the two nuclei were not bound together and the electron struck one nucleus, independent of the other. The limiting factor 4/3 indicates that, for small R_0, of the six degrees of freedom the three corresponding to the motion of the center of gravity and the one corresponding to vibration are excited, but not the two corresponding to rotation; for large R_0 the factor is 2, all six degrees of freedom are excited. The behavior of this ratio of total energy lost to the molecule, $\Delta E=(\Delta E)_{cg}+(\Delta E)_{rv}$ to the energy lost to motion of the center of gravity, $(\Delta E)_{cg}$, for intermediate values of (μ_0R_0), is given in Fig. 1.

When the incident electronic kinetic energy is small compared to $\hbar\omega$ only the rotational energies may be excited and the mean energy lost, in addition to $(\Delta E)_{cg}$, is

$$(\Delta E)_r\simeq\frac{2}{3}\frac{m}{M}(\tfrac{1}{2}mv^2)(1-\cos\vartheta) \times\left[\frac{1-j_0(\mu_0R_0)-j_2(\mu_0R_0)}{1+j_0(\mu_0R_0)}\right]. \tag{25}$$

For intermediate values of electronic energy the sum of $\hbar\omega n\sigma_n$ in the expression for ΔE must use Eq. (17) and be computed term by term.

These results indicate that the amount of energy lost to rotation-vibration of a gas molecule by a free electron is of the same order of magnitude as that lost to moving its center of mass, the ratio going from unity, for very slow electrons to two for faster ones and that appreciably larger amounts of energy are not lost until the electronic energy is large enough to excite the molecular electrons. This conclusion is probably a correct one, though the results worked out here do not include the effects of polarization. Inclusion of polarization is unlikely to change the vibration-rotation cross sections by a very large factor; it is more likely to affect the cross sections for electronic excitation, which appear for incident energies larger than those considered here. There is no indication of any sharp-peaked resonance effect in the energy region considered, nor, indeed, should one have been expected.

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Magnetic Structure Transitions*†

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The problem of magnetic phase transitions between ferromagnetism and antiferromagnetism, or between two different kinds of antiferromagnetic arrangement, is treated by a molecular field approach. It is shown that such transitions may occur if the molecular field coefficients vary with temperature; if they do occur, they will be of first order. The theoretical results agree qualitatively with the experimental results of Guillaud and Serres on MnAs.

THE Weiss molecular field treatment of ferromagnetism and antiferromagnetism has recently modified to include both first and second nearest neighbor interactions with all four combinations of signs.[1–3] One of the results of these investigations is that there are, in general, at least three possible types of magnetic ordering for a given magnetic lattice. They are ferromagnetic ordering and two types of antiferromagnetic ordering, one favoring antiferromagnetic arrangement of nearest neighbors and the second favoring antiferromagnetic arrangement of second nearest neighbors. The type of ordering which will actually occur is that with the highest Curie temperature and is determined by the signs and relative magnitudes of the interactions. In some instances, there is a critical value for the ratio γ_2/γ_1 (the Weiss field coefficients for first and second nearest neighbor interactions) such that the orderings on either side of this critical value are of different kinds. This result suggests that, in addition to the usual Curie temperature transitions, there may sometimes occur transitions in which the magnetic ordering changes from one kind to another. Moreover, there is excellent experimental evidence, owing to Guillaud[4] and Serres,[5] that transitions from a ferromagnetic to an antiferromagnetic arrangement occur in MnAs and MnBi. The purpose of this paper is to develop a simple theoretical model for such transitions. Garrett[6] and Ziman[7] have recently discussed the problem of phase transitions from an antiferromagnetic to a "ferromagnetic" state produced by a strong magnetic field. We shall discuss here, using a model similar to Garrett's, the possibility of changes in the type of magnetic ordering in zero applied field.

PROPERTIES OF A NORMAL FERROMAGNET OR ANTIFERROMAGNET

For simplicity, we consider a system of N atoms whose magnetic moments are due to a single unpaired spin on each atom. Let the atoms be arranged on a lattice which may be divided into n sublattices in such a way that a given atom has neither first nor second nearest neighbors on its own sublattice and only one kind of neighbors on any other sublattice. Let γ_1 and γ_2 be the Weiss field coefficients for first and second nearest neighbor interactions. If we assume, as is usual, that the molecular field is an approximation to the effects of exchange coupling, then the γ_i are given by

$$\gamma_i = 2Z_i|J_i|/g\beta, \quad i=1, 2, \tag{1}$$

where Z_i is the number of ith nearest neighbors and J_i is the exchange interaction between electrons on ith neighbors; β is the Bohr magneton and g the gyromagnetic ratio of the electron. Then the molecular field $\mathbf{H}_{jk}$ acting on an atom on the jth sublattice due to its neighbors on the kth sublattice is

$$\mathbf{H}_{jk} = \epsilon_{jk}\gamma_{jk}\mathbf{S}_k, \tag{2}$$

where ϵ_{jk} is $+1$ or -1 depending on whether the $j-k$ interaction is ferromagnetic or antiferromagnetic, γ_{jk} is

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