

been reduced to  $10^{-7}$  mm by a day's pumping, the deterioration of the potassium occurred much more slowly, and decay in detected signal attributable to coating of the platinum filament was virtually nonexistent. It may be concluded that the partial pressures of non-noble gases had been reduced to very low levels.

#### ACKNOWLEDGMENT

The authors are very much indebted to Mr. L. Wallace of Lockheed Missile and Space Division for his assistance in the fabrication of the experimental apparatus and for his aid in performing the measurements.

## Image of the Fermi Surface in Spin-Wave Spectra of Rare-Earth Metals\*

EDWIN J. WOLL, JR.,† AND STEPHEN J. NETTEL

*Department of Physics, University of California, San Diego, California*

(Received March 20, 1961)

Calculations of spin-wave spectra in rare earth metals were carried out to find whether images of the electronic Fermi surface might be observable. In the space of spin-wave vectors  $\mathbf{q}$  there should occur surfaces on which the frequencies have an infinite gradient with respect to  $\mathbf{q}$ , the location of such abrupt changes, "kinks" in the dispersion curves, being determined by the shape of the Fermi surface. The spin-wave spectrum is found by assuming that the coupling between ionic spins takes place primarily through exchange scattering of conduction electrons, paralleling the calculation on the coupling of nuclear spins by Ruderman and Kittel. Spin-wave dispersion curves in two directions of high symmetry are computed numerically. The sought-for kinks in the dispersion curves are found to amount to about 2% of the maximum excitation frequency. The development is for ferromagnets, but extension to spiral antiferromagnets is taken up briefly.

### I. INTRODUCTION

THE suggestion has been made by Kohn that, because of screening of the ions in a metal by conduction electrons, images of the electronic Fermi surface might show up in the phonon spectrum.<sup>1</sup> Kohn also pointed out that a similar effect might exist for spin waves in cases where the interaction between ionic spins originates primarily from exchange scattering with the conduction electrons.<sup>2</sup> In the space of wave vectors, for either of these excitations there will occur certain surfaces on which the frequencies will vary rather abruptly with  $\mathbf{q}$ ; the location of these surfaces will be determined by the shape of the Fermi surface. This raises the possibility of obtaining direct experimental information about the Fermi surface by examining these spectra, for example, with neutron scattering techniques.

For phonons special considerations, which will be discussed in a later publication, cause the effect to be so small as, probably, to be unobservable at present. A study of spin waves in the rare-earth metals, which will be the subject of the present paper, leads to more encouraging results.

The calculation of the spin-wave spectrum is similar to that carried out by Kasuya.<sup>3</sup> In view of the small radius of the  $4f$  shell in the rare-earth metals the lattice spins are assumed to be coupled primarily through ex-

change scattering of conduction electrons.<sup>3,4</sup> A quasi-Hamiltonian describing the interaction of any two lattice spins is obtained, first, by choosing suitable interaction potentials between otherwise free conduction electrons and individual lattice spins. The change in total energy is then found by a perturbation calculation carried out to second order, paralleling the calculation on the coupling of nuclear spins by Ruderman and Kittel.<sup>2</sup> This leads to the familiar Heisenberg scalar-product interaction for the lattice spins. The spin-wave excitations are found in the usual way by expanding the Hamiltonian in powers of  $1/S$ .<sup>3,5</sup>

Since the rare-earth metals of interest have hexagonal close-packed (hcp) structure, that is, they have two atoms per unit cell, an additional transformation is required to diagonalize the Hamiltonian. Approximate numerical calculations of the spin wave frequencies as functions of the propagation vector  $\mathbf{q}$  in two directions of high symmetry are carried out, so that the magnitudes of the expected discontinuities can be determined. Throughout the development the assumption is made that the ground state of the crystal is ferromagnetic. The extension of these results to the antiferromagnetic case is taken up briefly in the final discussion.

### II. THE CALCULATION

In view of the small radius of the ions, the interaction between a conduction electron and the ionic

\* Supported in part by the Office of Naval Research.

† National Science Foundation Predoctoral Fellow at the Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

<sup>1</sup> W. Kohn, Phys. Rev. Letters **2**, 393 (1959).

<sup>2</sup> M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954).

<sup>3</sup> T. Kasuya, Progr. Theoret. Phys. (Kyoto) **16**, 58 (1956).

<sup>4</sup> P.-G. de Gennes, Compt. rend. **247**, 1836 (1958).

<sup>5</sup> T. Holstein and H. Primakoff, Phys. Rev. **58**, 1098 (1940).

spins is chosen to have a Dirac delta function spatial dependence. The interaction can be written as

$$H' = G \sum_i \delta(\mathbf{R}_i - \mathbf{r}_e) \mathbf{J}_i \cdot \mathbf{S}_e. \quad (1)$$

Here  $\mathbf{J}_i$  and  $\mathbf{S}_e$  are the angular momentum of the lattice ion, and electron spin operators.  $\delta(\mathbf{R}_i - \mathbf{r}_e)$  is a delta function of the displacement of the electron relative to the position  $\mathbf{R}_i$  of the ion  $i$ . The summation runs over the  $N$  ions of the lattice.  $G$  is the coupling constant of the metal under consideration. The scalar product form  $\mathbf{J}_i \cdot \mathbf{S}_e$  appearing in the interaction has been discussed by Kasuya<sup>3</sup> and by Liu.<sup>6</sup> The interaction (1) has been postulated by de Gennes and Friedel<sup>7</sup> in their calculation of the resistivity of gadolinium. They were able to deduce an approximate value for the coupling constant  $G$  from experimental resistivities. de Gennes has suggested that for the series of rare-earth metals from Gd to Tu the coupling constant  $G$  can be taken proportional to  $(g-1)J$ , where  $g$  is the Landé factor.<sup>4</sup>

To second order in the interaction (1), the effective Hamiltonian for the lattice spins is<sup>2</sup>

$$H_{\text{eff}} = (G^2/2) \sum'_{i,j} \mathbf{J}_i \cdot \mathbf{J}_j F(\mathbf{R}_i - \mathbf{R}_j). \quad (2)$$

Here the sum runs over all lattice spins  $i$  and  $j$ , terms for which  $i$  is equal to  $j$  being omitted.  $F(\mathbf{R}_i - \mathbf{R}_j)$  is the well-known long-range oscillating interaction introduced by Ruderman and Kittel, and is given by

$$F(\mathbf{R}_i - \mathbf{R}_j) = V^{-2} \sum_{\mathbf{k}, \mathbf{k}'} (2m^*/\hbar^2) (k^2 - k'^2)^{-1} \times e^{i(\mathbf{k}' - \mathbf{k}) \cdot (\mathbf{R}_i - \mathbf{R}_j)}. \quad (3)$$

The sum in (3) runs over all occupied electronic states of momentum  $\hbar\mathbf{k}$ , and over all unoccupied states of momentum  $\hbar\mathbf{k}'$ .  $V$  is the volume of the crystal, and  $m^*$  the effective mass of the conduction electrons.

The next step is to substitute into (2) the Holstein-Primakoff operators  $a_i^*$ ,  $a_i$ , defined by<sup>5</sup>

$$\begin{aligned} (2J)^{\frac{1}{2}} \left( 1 - \frac{a_i^* a_i}{2J} \right)^{\frac{1}{2}} a_i &= J_{ix} + iJ_{iy}, \\ (2J)^{\frac{1}{2}} a_i^* \left( 1 - \frac{a_i^* a_i}{2J} \right)^{\frac{1}{2}} &= J_{ix} - iJ_{iy}, \\ J - a_i^* a_i &= J_{iz}. \end{aligned} \quad (4)$$

The resulting expression is expanded in powers of  $1/J$ , giving

$$H_{\text{eff}} = (G^2/2) J^2 \sum'_{i,j} F(\mathbf{R}_i - \mathbf{R}_j) \times \left[ 1 + \frac{2}{J} (-a_i^* a_i + a_i^* a_j) \right]. \quad (5)$$

Higher order terms with three or more operators represent interactions between spin waves, and are omitted.<sup>5</sup>

As already noted, the rare-earth metals of interest have hcp structure. The lattice ions can, accordingly, be regarded as lying on two hexagonal Bravais lattices, whose relative displacement will be denoted by the vector  $\mathbf{D}$ . The position vector of any ion on the first lattice will continue to be written as  $\mathbf{R}_i$ ,  $i=1, 2, \dots, N/2$ , and the corresponding spin operators  $a_i^*$ ,  $a_i$  will be written as  $a_i^{*(e)}$ ,  $a_i^{(e)}$ . For the second lattice the positions and spin operators will be  $(\mathbf{R}_i + \mathbf{D})$ , and  $a_i^{*(0)}$ , and  $a_i^{(0)}$ . The transformations to be substituted into (5) are then

$$\begin{aligned} a_i^{(e)} &= (2/N)^{\frac{1}{2}} \sum_q \exp[i\mathbf{q} \cdot \mathbf{R}_i] a_q^{(e)}, \\ a_i^{(0)} &= (2/N)^{\frac{1}{2}} \sum_q \exp[i\mathbf{q} \cdot (\mathbf{R}_i + \mathbf{D})] a_q^{(0)}. \end{aligned} \quad (6)$$

Here  $\sum_q$  indicates a sum over all wave vectors lying in the first Brillouin zone of the hexagonal Bravais lattice. Omitting the  $J^2$  term in (5), one gets

$$H_{\text{eff}} = G^2 J \sum_q [A_q (a_q^{*(e)} a_q^{(e)} + a_q^{*(0)} a_q^{(0)}) - B_q a_q^{*(e)} a_q^{(0)} - B_q^* a_q^{*(0)} a_q^{(e)}], \quad (7)$$

where

$$A_q = -\sum_{\mathbf{R}} [F(\mathbf{R}) + F(\mathbf{R} + \mathbf{D}) - \exp(i\mathbf{q} \cdot \mathbf{R}) F(\mathbf{R})], \quad (8a)$$

and

$$B_q = -\sum_{\mathbf{R}} \exp[i\mathbf{q} \cdot (\mathbf{R} + \mathbf{D})] F(\mathbf{R} + \mathbf{D}). \quad (8b)$$

Here the sums run over all the relative displacements  $\mathbf{R}$  of a single Bravais lattice, including  $\mathbf{R} = 0$ .

Finally, to diagonalize (7) one uses the substitutions

$$\begin{aligned} b_q &= 2^{-\frac{1}{2}} [a_q^{(e)} + \alpha_q (\alpha_q \alpha_q^*)^{-\frac{1}{2}} a_q^{(0)}], \\ c_q &= 2^{-\frac{1}{2}} [a_q^{(e)} - \alpha_q (\alpha_q \alpha_q^*)^{-\frac{1}{2}} a_q^{(0)}], \\ \alpha_q &= B_q / A_q. \end{aligned} \quad (9)$$

The result is

$$H_{\text{eff}} = G^2 J \sum_q \{ b_q^* b_q [A_q - (B_q B_q^*)^{\frac{1}{2}}] + c_q^* c_q [A_q + (B_q B_q^*)^{\frac{1}{2}}] \}. \quad (10)$$

For simplicity this study will be restricted to the "acoustical" spin waves, whose frequencies  $\omega_q$  are given by

$$\hbar\omega_q = G^2 J [A_q - (B_q B_q^*)^{\frac{1}{2}}]. \quad (11)$$

To carry out the computations one needs to define the Fourier transform,  $f(\mathbf{p})$ , of  $F(\mathbf{R}_i - \mathbf{R}_j)$ :

$$F(\mathbf{R}_i - \mathbf{R}_j) = V^{-1} \sum_{\mathbf{p}} f(\mathbf{p}) \exp[i\mathbf{p} \cdot (\mathbf{R}_i - \mathbf{R}_j)], \quad (12a)$$

where from (3)

$$f(\mathbf{p}) = -(2m^*/\hbar^2) V^{-1} \sum_{\mathbf{k}} (p^2 + 2\mathbf{p} \cdot \mathbf{k})^{-1}. \quad (12b)$$

The sum in (12b) runs over all occupied electronic states  $\mathbf{k}$ . These are assumed to occupy a sphere in reciprocal space of radius  $k_F$ , where  $\hbar k_F$  is the Fermi

<sup>6</sup> S. H. Liu, Phys. Rev. **121**, 451 (1961).

<sup>7</sup> P.-G. de Gennes and J. Friedel, J. Phys. Chem. Solids **4**, 71 (1958).

momentum.<sup>8</sup> A straightforward integration yields

$$f(\mathbf{p}) = \frac{-m^*k_F}{8\pi^2\hbar^2} \left[ 1 + \frac{1}{2} \left( \frac{2k_F}{p} - \frac{p}{2k_F} \right) \ln \left| \frac{p+2k_F}{p-2k_F} \right| \right]. \quad (13)$$

A plot of the function  $f(\mathbf{p})$  is shown in Fig. 1. It should be noted that the derivative of  $f(\mathbf{p})$  has a logarithmic infinity at  $p=2k_F$ .

When the lattice sums indicated in Eqs. (8a) and (8b) are carried out with the help of the transform (12a), one finds that

$$A_q = -\frac{N}{2V} \sum_{\mathbf{K}} [f(\mathbf{K}) - f(\mathbf{K}+\mathbf{q}) + f(\mathbf{K}) \cos(\mathbf{K} \cdot \mathbf{D})], \quad (14a)$$

$$B_q = -\frac{N}{2V} \sum_{\mathbf{K}} [f(\mathbf{K}+\mathbf{q}) \exp(i\mathbf{K} \cdot \mathbf{D})]. \quad (14b)$$

The sums run over all reciprocal vectors  $\mathbf{K}$  of the Bravais lattice. Use has been made of the fact that  $f$  is even in  $\mathbf{p}$ .

The spin-wave frequencies  $\omega_q$  are calculated by substituting Eqs. (13), (14a), and (14b) into Eq. (11). The reciprocal vectors of a hexagonal lattice also form a hexagonal lattice. For spin wave vectors  $\mathbf{q}$  pointing in the direction of the  $c$  axis in reciprocal space, the formula for the acoustical frequencies takes the particularly simple form:

$$\hbar\omega_q = -G^2J \frac{N}{2V} \sum_{\mathbf{K}} [f(\mathbf{K}) - f(\mathbf{K}+\mathbf{q})] \times [1 + \cos(\mathbf{K} \cdot \mathbf{D})]. \quad (15)$$

Approximate numerical calculations of the dispersion curve in the directions of the  $c$  axis and of the  $a$  axis have been carried out. The results are shown in Fig. 2. In finding the frequencies, discrete sums over the first 307 points in reciprocal space were taken. The sum  $\sum_{\mathbf{K}} [f(\mathbf{K}) - f(\mathbf{K}+\mathbf{q})] \exp(i\mathbf{K} \cdot \mathbf{D})$  was found to converge sufficiently rapidly that more distant points could be neglected. The sum  $\sum_{\mathbf{K}} [f(\mathbf{K}) - f(\mathbf{K}+\mathbf{q})]$  over the more distant points was approximated by a suitable integral.

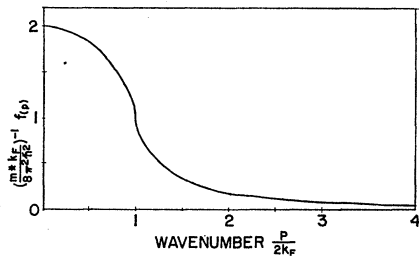


FIG. 1. Plot of Fourier transform  $f(\mathbf{p})$  of the range function  $F(\mathbf{R}_i - \mathbf{R}_j)$ . Note infinite slope at  $p/2k_F$  equal to unity.

<sup>8</sup> Inclusion in the sum of states  $\mathbf{k}$  for which states  $\mathbf{k}'$  ( $\mathbf{k}' = \mathbf{k} + \mathbf{p}$ ) are also occupied does not affect the result.

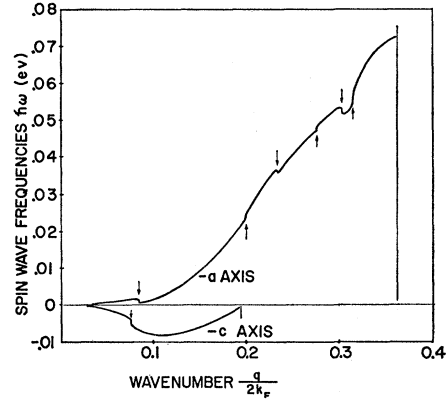


FIG. 2. Calculated spin-wave dispersion curves in high-symmetry directions. Fermi images are indicated by arrows. Frequency values are calculated using the coupling constant  $G$  for gadolinium, derived from the observed resistivity;  $m^*$  is taken to be the free electron mass. Frequencies for other rare-earth metals can be obtained by multiplying by  $(g-1)J/7.5$ .

### III. DISCUSSION

A Fourier component  $f(\mathbf{K}+\mathbf{q})$  undergoes an abrupt change with  $\mathbf{q}$  whenever

$$|\mathbf{q} + \mathbf{K}| = 2k_F, \quad (16)$$

as already mentioned. Consequently, a "kink" occurs in the spin-wave dispersion curves at every vector  $\mathbf{q}$  that satisfies Eq. (16) with any one of the reciprocal lattice vectors  $\mathbf{K}$ .<sup>9</sup> From the calculations one sees that these kinks, marked by arrows in Fig. 2, are of the order of 2% of the maximum excitation frequencies. They would appear, therefore, to be within the range of experimental detection.

It will be observed that the frequencies become negative for  $\mathbf{q}$  in the  $c$  direction. The calculations have shown that the frequencies are extremely sensitive in magnitude and sign to small changes in the location of the Fermi surface. However, the magnitude of the kinks is not seriously affected by such changes. When for some frequencies the dispersion curve becomes negative, the ground state of the crystal is no longer ferromagnetic; rather, it corresponds to an antiferromagnetic spiral structure with a pitch that can in principle be deduced from what is essentially the negative "dispersion curve."<sup>10,11</sup> Some of the rare-earth metals have, in fact, been observed to have spiral antiferromagnetic structures.<sup>12</sup> The sensitivity of the dispersion curves, already suggested by the disparity between the two curves of Fig. 2, may help to explain some of the remarkable magnetic properties of the rare-earth metals.<sup>12</sup>

<sup>9</sup> When the Fermi surface is not spherical, (16) must be replaced by Eq. (10) of reference 1.

<sup>10</sup> J. Villain, J. Phys. Chem. Solids **11**, 303 (1959).

<sup>11</sup> K. Yosida and H. Miwa, Technical Report of Institute for Solid-State Physics, Ser. A, No. 14, University of Tokyo, Tokyo, Japan (unpublished).

<sup>12</sup> B. L. Rhodes, S. Legvold, and F. H. Spedding, Phys. Rev. **109**, 1547 (1958). See also W. C. Koehler *et al.*, Rare-Earth Research Developments Conference, University of California, Lake Arrowhead, California (unpublished), Sec. II.

The present results are applicable to rare-earth metals only when in a ferromagnetic state, either naturally or under the action of a strong magnetic field.<sup>12</sup> For spiral antiferromagnetic structures of crystals with only one atom per unit cell, Kasuya as well as Yosida has found a spin-wave spectrum give by<sup>11</sup>

$$\hbar\omega_q \propto 2J[\{d - I(\mathbf{q}) + I(\mathbf{q}_0)\} \times \{I(\mathbf{q}) - \frac{1}{2}I(\mathbf{q}_0 + \mathbf{q}) - \frac{1}{2}I(\mathbf{q}_0 - \mathbf{q})\}]^{\frac{1}{2}}, \quad (17)$$

where  $d$  is a constant used to describe anisotropy energy in the hard direction of magnetization, i.e., is positive, and  $I(\mathbf{q})$  is directly proportional to  $\sum_{\mathbf{K}} [f(\mathbf{K}) - f(\mathbf{K} - \mathbf{q})]$  in the present notation.  $\mathbf{q}_0$  gives the pitch of the ground-state spiral structure. Formula (17) indicates that in the spin-wave spectra of antiferromagnetic structures images of the Fermi surface such as found in the ferromagnetic case will appear, and with comparable magnitudes. The condition for a kink is that the vector  $\mathbf{q}$  satisfy any one of the conditions:

$$|\mathbf{q} + \mathbf{K}| = 2k_F, \quad |\mathbf{q} + \mathbf{q}_0 + \mathbf{K}| = 2k_F, \quad |\mathbf{q} - \mathbf{q}_0 + \mathbf{K}| = 2k_F, \quad (18)$$

where  $\mathbf{K}$  is again any one of the reciprocal lattice vectors.

In conclusion, a few remarks about the effect of the finite size of the ion core are in order. These are extremely difficult to treat quantitatively. However, it should be noted that to some extent these effects are allowed for in the determination of the constant  $G$  from observed resistivities, and that the dimensionless parameter that measures the importance of these effects, namely  $k_F r_0$ , where  $r_0$  is the "radius" of the ion cores, has a value of 0.4. It is, therefore, not to be expected that the estimate of the relative size of the kinks given here is significantly in error.

#### ACKNOWLEDGMENTS

This investigation was suggested to us by Professor Walter Kohn. We are much indebted to Professor Kohn for his continued interest and assistance. We would also like to thank Professor H. Suhl and Dr. J. Des Cloizeaux for helpful discussions.

## Photosensitive-Ultrasonic Properties of Cadmium Sulfide

HARMON D. NINE

*General Motors Research Laboratories, Warren, Michigan*

AND

ROHN TRUETT\*

*Brown University, Providence, Rhode Island*

(Received January 9, 1961)

Ultrasonic attenuation in single crystals of CdS has been observed to be a function of light irradiation. Two distinct types of behavior have been observed. Some crystals (type A) show a decrease of attenuation with white light application, and others (type B) show an increase of attenuation with white light. The ultrasonic attenuation and the conductance of the crystals were measured as a function of temperature. An excellent correlation between the conductance and the ultrasonic attenuation is evident for type B crystals. A strong correlation between the directional piezoelectric properties of CdS and the ultrasonic attenuation in both types of CdS is also shown. An interaction between conduction electrons and stress waves coupled by the piezoelectric property of CdS is isolated as the dominant mechanism for the photosensitive ultrasonic attenuation in CdS of type B. Two or more competing effects appear to be responsible for the type A photosensitive attenuation behavior.

#### INTRODUCTION

**I**N a previous paper by one of the authors it has been observed that there are pronounced changes in the ultrasonic attenuation in single-crystal samples of CdS when such samples are exposed to light over the spectral range from the band edge at 5100 to 8000 Å.<sup>1</sup> In that paper, two distinct effects of light irradiation on the

ultrasonic attenuation in different CdS crystals, called type A and type B crystals, were discussed. Type A crystals showed a decrease of attenuation upon irradiation with light in the indicated spectral region and type B crystals showed an increase in attenuation upon irradiation. This paper describes recently completed work by the authors on the temperature variation of both ultrasonic attenuation and electrical conductance and further work on the photosensitive attenuation as a function of crystal direction which has made it possible to isolate the mechanism primarily responsible

\* Some of the low-temperature measurements on cadmium sulfide were made at Brown University and in this connection acknowledgement of support is made to the National Science Foundation.

<sup>1</sup> H. D. Nine, *Phys. Rev. Letters* 4, 359 (1960).