Towards a Theory of the Anomalous Thermoelectric Effect in Magnetically Dilute Alloys*

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The low-temperature properties of alloys of the noble metals with low concentrations of transition metals show many anomalies, conspicuous among them relatively enormous thermoelectric powers and nonmonotonic behavior of the resistivity with temperature. We investigate to what extent these anomalies might be explained by supposing the existence of spiraling magnetic polarizations of the electron gas, i.e., static spin-density waves. We discuss qualitatively how thermoelectric anomalies can arise, first in terms of an earlier theory which requires weak ferromagnetism in the noble metals and then in terms of the spin-density-wave hypothesis, an assumption of weak antiferromagnetism. We solve the Boltzmann equation, including inelastic scattering, for the two theories and display the thermoelectric powers and resistivities as functions of the temperature. We consider several different models of spin-density-wave system, one appropriate to electron-electron interactions proportional to delta functions in the separation, another an approximation to Coulombic interelectron forces, and finally a linear spin-density wave as the simplest case of a multiple spin-density-wave configuration. We find that the spin-density-wave hypothesis can explain the magnitudes of the thermoelectric anomalies. Further, we find nonmonotonic resistivity behavior. A comparison with experiments shows that our model is too simple to provide a detailed explanation of the anomalous thermoelectricity and that the nonmonotonic resistivity we find cannot be associated with that observed experimentally.

INTRODUCTION

THE low-temperature behavior of the electron gas in dilute alloys of noble metals and transition metals has been a puzzle ever since the discovery by Borelius and co-workers of anomalous—"giant"—thermoelectric powers.[1] Subsequent experiments have revealed corresponding anomalies in a wide variety of alloy systems and many other electronic properties.[2]

Two aspects of the experiments are especially striking: (1) the anomalies occur—for some effects virtually unchanged in magnitude—for the lowest concentrations of the transition metal impurities that can be reliably determined, and (2) when different properties of an anomalous alloy system are measured, each property investigated shows an anomaly.

The nonmonotonic behavior of the resistivity of these alloy systems has attracted much experimental and theoretical attention. The experiments have indicated that the appearance of the anomalies depends in a crucial way on the existence of magnetic moments localized on the impurity ions,[3] and the theoretical studies have used this as a starting point.

The most difficult aspect of the resistivity-minimum data to understand are the measurements on alloys of extreme dilution, for in these, the resistivity is found to rise monotonically as absolute zero is approached. Two theories exist which predict this sort of behavior, one due to Brailsford and Overhauser[4] which predicts a $1/T$ dependence at low temperatures, the second a phenomenological discussion by Korringa and Gerritsen, given the form of a complete theory by Kondo,[5] in which the resistivity varies as $\log T$. The experiments favor the latter theory.

The thermoelectric anomaly has similarly attracted attention. The most nearly successful theory of the anomalies to date has evolved from a suggestion by Schmitt[6] that the transition metal impurities are magnetized in the host lattice and that the alloy system is weakly ferromagnetic. Three versions of this theory[7] have appeared, all substantially identical in

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content and results, differing only in technique and transparency; the first of these is due to Kasuya. This is the only published theory which produces thermoelectric powers of the order of magnitude of those seen experimentally in the appropriate temperature range.

The assumptions of the Kasuya theory are incompatible with those of the Kondo theory, and Kondo's theory (at least in its original form) is unable to explain the anomalous thermoelectric effect.[8] The temperature dependence of the resistivity in the Kasuya theory has been carefully examined by DeVroomen and Potters.[7] The resistivity, while affected by the magnetic scattering, shows nothing but monotonic behavior.

It has been shown that the anomalous specific heats may be understood on the basis of a spin-density-wave model.[9] We reported previously[10] that the model would also produce anomalous thermoelectric powers of the order of magnitude of experiment. We here further explore the consequences of this model. The thermoelectric power calculations which we discussed then are presented. In addition, calculations and results on the resistivity as a function of temperature are given. We find resistivity behavior which resembles that shown by some of the alloys of higher impurity concentration, a minimum followed by a maximum and then a steep drop as the temperature is lowered. Also, we find no resistivity rise at zero for any reasonable choice of parameters. A more extensive discussion of this calculation is available elsewhere.[11]

The point of view in Ref. 9 was that the spin-density wave in the conduction electrons was stabilized by the energy of interaction between electron-gas polarization and the magnetic moments of the impurities. The conventional picture of the ground state of the pure host was retained. The extremely low concentrations at which the thermoelectric anomaly is observed force us to a more radical hypothesis, that the ground states of the pure host materials have spin-density waves. The recent experiments of Kitchens, Steyert, and Taylor,[12] as well as Craig and Steyert[13] lend support to this notion.

We consider the ferromagnetic Kasuya model from a qualitative point of view in an effort to understand the physical origins of the giant thermoelectric effect. We shall find that we have simultaneously made clear the antiferromagnetic case.

We assume a set of one-electron states labeled by the wave number vector $\mathbf{k}$, with one-electron energy $E(\mathbf{k})$, and occupied with probability $f(\mathbf{k})$. With each state we associate a velocity, $\mathbf{v}(\mathbf{k})$. Let us call $f(\mathbf{k})$ in equilibrium $f_0(\mathbf{k})$; this will be the well-known Fermi function of $E(\mathbf{k})$.

The effect of an electric field is to distort the distribution function $f(\mathbf{k})$. This tendency is opposed by the scattering off impurities, and a steady state is maintained. In general, both the response of the distribution to the field and the effectiveness of the scattering in restoring the equilibrium value depend upon the state $\mathbf{k}$ in question. Where the scattering is relatively ineffective, the distortion in $f(\mathbf{k})$ will be large compared to $\mathbf{k}$'s for which the scattering is more effective. Our task is to assume a model for the scattering interaction and use this to find $f(\mathbf{k})$ from which we can easily find quantities like the electric current by summing over k space.

Our primary concern is with the thermoelectric power. Using Kelvin's second relation, we can write this as the ratio of the Peltier coefficient to the temperature, or as T^{-1} times the Peltier heat current divided by the electric current.

$$S=\kappa\frac{\sum_{\mathbf{k}} f(\mathbf{k})\mathbf{v}(\mathbf{k})\{[E(\mathbf{k})-\zeta]/\kappa T\}}{\sum_{\mathbf{k}} ef(\mathbf{k})\mathbf{v}(\mathbf{k})}. \tag{1}$$

ζ is the Fermi energy. The denominator of (1) is clearly equal to the electric current; the numerator is of the form of an excess (compared to ζ), relative (in units of κT) energy current.

In Fig. 1 we represent $f(\mathbf{k})$ for a very simple model of conduction; the equilibrium distribution is simply shifted along the direction of the electric field $\mathcal{E}$. The contribution of most of the occupied states to the sums in Eq. (1) is cancelled by opposite contributions of states symmetrically located. Only the states in the lens-shaped regions above and below ζ contribute to Eq. (1). The two lenses contain the same number of states (to order $\mathcal{E}^2$), and all the states have the same

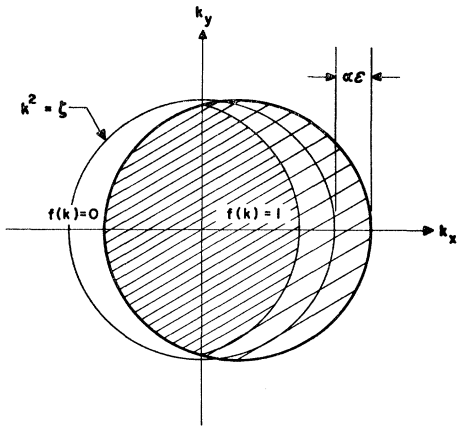

FIG. 1. A schema to represent the simplest aspects of electrical conduction.

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$v(\mathbf{k})$ (to order $\mathcal{E}$). But since $E(\mathbf{k})-\zeta$ is positive in the upper lens and negative in the lower, the contributions of the two lenses to the numerator of Eq. (1) are equal in magnitude and opposite in sign; the excess relative heat current vanishes (to order $\mathcal{E}$) and the thermoelectric power vanishes. At a higher temperature than that for which Fig. 1 is drawn, the limits of the distribution would be blurred instead of sharp and the cancellation would not be exact. This is the ordinary thermoelectric effect. The giant thermoelectric effect appears when the cancellation is disrupted.

The sums in Eq. (1) depend upon $E(\mathbf{k})$ and $v(\mathbf{k})$, which are relatively slowly varying with energy, and the departure of $f(\mathbf{k})$ from equilibrium values. It is clear that if our simple picture of the electrons is to lead to giant thermopowers, the distortion of $f(\mathbf{k})$, i.e., $\Delta f(\mathbf{k})$, must be different in the upper and lower lenses of Fig. 1. In other words, Δf must be a strongly varying, asymmetric function of the energy in the neighborhood of the Fermi surface. Δf is the resultant of two competing processes. The electric field exerts the same force on every electron of the assembly independent of its velocity and is hence unlikely to produce the necessary variation. This independence of velocity, together with an assumed independence of velocity of the scattering behavior lead to the simple model of Fig. 1. We look to more complicated scattering behavior to understand the giant effect.

The probability per unit time of a scattering event from a state $\mathbf{k}$ to a state $\mathbf{k}'$ is proportional to $f(\mathbf{k})\times[1-f(\mathbf{k}')]$ just on the basis of the statistics of electrons. Let us call the remaining factor $W(\mathbf{k}'\mathbf{k})$.

$$dP(\mathbf{k}'\mathbf{k})/dt=W(\mathbf{k}'\mathbf{k})f(\mathbf{k})[1-f(\mathbf{k}')]. \quad (2)$$

$W(\mathbf{k}'\mathbf{k})$ depends on the energy difference of the initial and final states through energy conservation. If, in addition, the scattering mechanism made $W(\mathbf{k}'\mathbf{k})$ strongly dependent on the initial state energy and asymmetric about E_F, we would need to look no further for the source of the anomaly. Such a dependence is very difficult to justify. For the purposes of this discussion, we shall ignore the dependence of W on the initial state energy.

We may write the expression Eq. (2) as a sum of an equilibrium part, a higher order part which we throw away, and a term of the order of Δf:

$$W(\mathbf{k}'\mathbf{k})\{f_0(\mathbf{k})[1-f_0(\mathbf{k}')] +\Delta f(\mathbf{k})[1-f_0(\mathbf{k}')]-f_0(\mathbf{k})\Delta f(\mathbf{k}')\}. \quad (3)$$

That in equilibrium there is no net transfer from $\mathbf{k}$ to $\mathbf{k}'$ implies

$$W(\mathbf{k}'\mathbf{k})=e^{-[E(\mathbf{k}')-E(\mathbf{k})]/\kappa T}W(\mathbf{k}\mathbf{k}')\equiv e^{-\mu}W(\mathbf{k}\mathbf{k}'), \quad (4)$$

leaving for the net transfer rate from state $\mathbf{k}$ to $\mathbf{k}'$

$$W(\mathbf{k}'\mathbf{k})\{\Delta f(\mathbf{k})[1-f_0(\mathbf{k}')+e^{+\mu}f_0(\mathbf{k}')] -\Delta f(\mathbf{k}')[f_0(\mathbf{k})+e^{+\mu}(1-f_0(\mathbf{k}))]\}. \quad (5)$$

If the scattering is purely elastic, then $e^{+\mu}=1$, and the net scattering rate is just the slowly varying $W(\mathbf{k}'\mathbf{k})$ multiplied by the difference $\Delta f(\mathbf{k})-\Delta f(\mathbf{k}')$. This leads to the symmetrical Δf which was the basis of Fig. 1 and produces no anomaly.

If the scattering is inelastic, however, then (5) is composed of two terms

$$W(\mathbf{k}'\mathbf{k})\{\Delta f(\mathbf{k})e^{+\mu}Q(x,\mu)-\Delta f(\mathbf{k}')Q^{-1}(x,\mu)\};\quad x=[E(\mathbf{k})-\zeta]/\kappa T, \quad (6)$$

where $Q(x,\mu)=(e^x+1)/(e^{x+\mu}+1)$. The function Q which multiplies $W(\mathbf{k}'\mathbf{k})$ in (6) is not symmetrical about the Fermi energy. It changes from unity to $e^{+\mu}$ within a few ΔE of the Fermi surface. In effect, the inelasticity has made $W(\mathbf{k}'\mathbf{k})$ a rapidly varying, asymmetric function about ζ.

The mere fact of the presence of inelastic scattering, however, is not enough to insure that Δf will be distorted in the necessary way. The total scattering rate out of the state $\mathbf{k}$, the property which determines how large $\Delta f(\mathbf{k})$ will be, requires summing Eq. (6) over all final states $\mathbf{k}'$. Let us consider, then, the effect of scattering to states both higher and lower in energy than $\mathbf{k}$. The first term in Eq. (6) gives us

$$[W(\mathbf{k}\mathbf{k}')Q(x,\mu)+e^{-\mu}W(\mathbf{k}''\mathbf{k})Q(x,-\mu)]\Delta f(\mathbf{k}). \quad (7)$$

We rewrote the W factor referring to one of the scattering processes using Eq. (4). Now both of the W's in (7) refer to processes where the initial- and the final-state energies have the same separation. Since we are assuming that the basic scattering process is only weakly dependent on the initial-state energy, $W(\mathbf{k}\mathbf{k}')$ and $W(\mathbf{k}''\mathbf{k})$ are very nearly equal. But the remaining factor in (7), $Q(x,\mu)+e^{-\mu}Q(x,-\mu)$, is symmetrical about the Fermi energy and cannot lead to an asymmetrical Δf. The argument for the second term of (6) is similar. To obtain a thermoelectric anomaly, therefore, there must be something different about energy gaining and energy losing scattering processes.

A model in which there was only one kind of collision, energy gaining or losing, would certainly destroy the symmetry, but would be very difficult to justify. A model almost as good is one for which the electrons are divided into two groups, A and B. The scattering from A to B always involves an energy gain; scattering from B to A always involves an energy loss.

The introduction of this difference does indeed produce a Δf which is strongly varying and asymmetrical about ζ. However, if the two groups of electron states have the same energy and velocity functions and are alike except for the inelastic scattering behavior, the distortion in Δf about ζ for one group will be precisely opposite to the distortion for the other. The two groups will contribute equally and with opposite sign to the numerator in Eq. (1).

The final requirement of a model producing an anomalous thermoelectric power is that the two groups

between which the scattering is of "one-way" character shall not otherwise be identical.[14]

The ferromagnetic model of a dilute alloy satisfies all these criteria. The two groups are the spin-up and the spin-down electrons. When a spin-up electron scatters inelastically off a magnetized impurity ion, its spin is flipped down and the ion moment is flipped upwards. Because of the assumed internal field aligning the impurity moments, energy must be transferred to the ion in this process. In becoming a spin-down electron, the electron has lost energy. In the reverse process, a spin-down electron becomes a spin-up electron and gains energy from the ion. The number of spin-up and spin-down electrons is very nearly the same, and the energy and velocity functions are also alike. However, the elastic scattering of the electrons depends on whether they are aligned with the impurity or antialigned. The elastic-scattering rate is different for spin-up and spin-down electrons through the interference between spin-independent and S_z-dependent scattering. The conditions for a thermoelectric anomaly are satisfied.

To consider the case of antiferromagnetism, we need to understand the response of the electron gas to a field—or effective field—with an oscillating character. We shall consider the simplest case, a field of constant magnitude whose direction rotates as a function of position. The field as a function of position is described by

$$\mathbf{H}=H_0(\mathbf{l}_x \cos 2\mathbf{q}\cdot\mathbf{r}+\mathbf{l}_y \sin 2\mathbf{q}\cdot\mathbf{r});\quad \mathbf{l}_x\cdot\mathbf{r}\equiv x,\quad \mathbf{l}_y\cdot\mathbf{r}\equiv y. \tag{8}$$

The one-electron Hamiltonian is modified by the addition of a term

$$\mu H_0(\sigma_x \cos 2\mathbf{q}\cdot\mathbf{r}+\sigma_y \sin 2\mathbf{q}\cdot\mathbf{r}) = \mu H_0(\sigma^+ e^{-2i\mathbf{q}\cdot\mathbf{r}}+\sigma^- e^{2i\mathbf{q}\cdot\mathbf{r}}). \tag{9}$$

For most of the states of the electron gas, the additional term makes only a slight difference. It couples a state $\mathbf{k}\downarrow$ to a state $(\mathbf{k}-2\mathbf{q})\uparrow$. Notice that it does not couple a state $\mathbf{k}\uparrow$ with a state $(\mathbf{k}-2\mathbf{q})\downarrow$. It is this feature that makes the spiral the simplest antiferromagnetic configuration to deal with, for the Schrödinger equation including Eq. (8) can be solved exactly.

The states which are strongly influenced by the spiraling potential cannot be characterized as spin up or spin down in terms of the quantization axis used in the absence of the coupling. Their spins have a spiraling character with the same period as the spiraling field.

Figure 2 is a representation of the Fermi surface of an electron gas, both for spin-up and spin-down states, showing the modification of the energy surfaces caused by the spiraling field. The energy gaps are characteristics of a periodic potential; they do not occur symmetrically because the state $\mathbf{k}$ is not coupled symmetrically with the states $\mathbf{k}\pm 2\mathbf{q}$ as we mentioned.

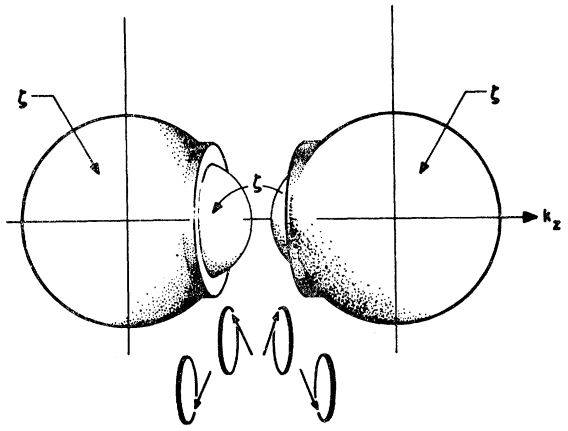

FIG. 2. The Fermi surfaces—spin up and spin down—for a gas of otherwise free electrons supporting a spin-density wave.

Every electron of the distribution has at least some spiraling character to its spin, although only those states close to the gaps are profoundly affected. All the states of the lower branch of the distribution, the truncated spheroids of Fig. 2, have their spiraling components in phase with the spiraling field. All the states of the upper branch have their spiraling components π out of phase with it. The lower states are lined up with the field at every point and the upper states are antialigned.

The states exactly on the faces of the gaps have their spins completely polarized by the spiraling field; they are completely "down" or "up" with respect to the field, those of the lower branch being down. A magnetized impurity ion will line up with the direction of the field at its site. Hence the same group of electron states will always be "up" or "down" with respect to every ion in the crystal. The states away from the gaps are neither purely "up" nor "down," but all of the lower branch states are more down than up, and all the upper branch states are more up. There will obviously be great differences in Fermi velocity, in the density of states, in the elastic scattering, and all the other properties of the states, between the upper and lower branch states. If we regard the upper and lower branches as the A and B groups of the previous discussion, it is clear that all the elements of a thermoelectric anomaly are present.

For a sufficiently large value of q or H_0, there may be no sheet of the Fermi surface in the upper states. The scattering from states near the gap, which are fully polarized, to states far from the gap, which are half "up" and half "down" with respect to the ions, has the "one-way" character necessary for the production of a thermoelectric anomaly. Electrons can scatter from the gap to the "bulges" only by turning an impurity spin down, and in reverse only by turning the

[14] A. M. Guenault and D. K. C. MacDonald, Phil. Mag. 6, 1201 (1961).

spin up. There is no inelastic scattering between states close to the gap because they are all "down."

There is inelastic scattering among the states of the "bulges." Also there is elastic scattering between the gaps and the bulges. Finally, the bifurcation into two groups is not sharp; the polarized character of a state changes gradually as one approaches a gap. These features are not shared by the ferromagnetic model, where the division into two groups is sharp, where inelastic scattering occurs only within groups. However, it is clear that the antiferromagnetic model of an electron gas can produce anomalies in the thermoelectric effect, reduced, perhaps in magnitude.

Ferromagnetism and the spiraling antiferromagnetism are examples of long-range ordering. If we admit the simultaneous presence of several or many spin-density waves (SDW), a single-spin-density wave appears as nothing more than a Fourier component of a general electron magnetization. If the impurity spins are random, it will take a great many components with $\mathbf{q}$ vectors of many orientations to describe the structure. As a result, it will be impossible to perform the division of the electron states into two groups with one-way inelastic scattering. Under these circumstances, there will be no thermoelectric anomaly; this is a paramagnet, however, not an antiferromagnet.

The important question in applying these considerations to real situations such as dilute alloys is whether or not there is any reason to believe that a single-spin-density wave, or a limited number of them, should be of exceptional importance. This question is of interest quite apart from its relevance to the understanding of conduction anomalies. As a working hypothesis we assume an affirmative answer and show that the resulting thermoelectric power is large enough to explain the experimental anomalies.

We calculate the thermoelectric power and the conductivity of a gas of free electrons scattering from magnetized, localized impurities. We shall consider a simple spiral-spin-density wave in two models of the electron-electron interaction, treated in the framework of the Hartree-Fock approximation, the Boltzmann equation, and first-order time-dependent perturbation theory. We shall also consider an example of a multiple spin-density-wave state, the linear SDW which can be resolved into two spirals.

COMPUTATIONS

Our calculation of the transport properties is quite simple in structure, complicated only by the awkwardness introduced into the expressions by the form of the SDW one-electron wave functions and the associated nonsphericity of the Fermi surface. We write the Boltzmann equation

$$-e\mathcal{E}\cdot\nabla_k f_0(\mathbf{k})=(df/dt)_{\text{collisions}}, \tag{10}$$

and linearize it so that the collision terms become

$$\left(\frac{df}{dt}\right)_{\text{coll.}}=\sum_{\mathbf{k}'}[W(\mathbf{k}\mathbf{k}')\{\Delta f(\mathbf{k}')[1-f_0(\mathbf{k})]-f_0(\mathbf{k}')\Delta f(\mathbf{k})\}$$
$$-W(\mathbf{k}'\mathbf{k})\{\Delta f(\mathbf{k})[1-f_0(\mathbf{k}')]$$
$$-f_0(\mathbf{k})\Delta f(\mathbf{k}')\}],$$
$$f_0(\mathbf{k})\equiv\frac{1}{\exp([E_{\mathbf{k}}-\zeta]/\kappa T)+1}. \tag{11}$$

$W(\mathbf{k}\mathbf{k}')$ is evaluated by use of the Fermi "golden rule" of first-order time-dependent perturbation theory. With a few minor approximations which clearly do no violence to the physics, we can solve Eq. (10) for $\Delta f(\mathbf{k})$. With this distribution function, the sums in Eq. (1) are evaluated and the conductivity and thermoelectric power obtained. The operations are all elementary.

Let us begin with a description of the electrons. If we assume a one-electron potential of the form

$$d(\mathbf{k})+\epsilon(\mathbf{k})\sigma_z+c(\mathbf{k})[\sigma^+e^{-2i\mathbf{q}\cdot\mathbf{r}}+\sigma^-e^{2i\mathbf{q}\cdot\mathbf{r}}], \tag{12}$$

we may easily find eigenfunctions

$$\psi_{\mathbf{k}}=(1/\sqrt{\Omega})e^{i[E(\mathbf{k})+d(\mathbf{k})]t}$$
$$\times[A_1(\mathbf{k})e^{i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}}\alpha+A_2(\mathbf{k})e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}}\beta],$$
$$A_1(\mathbf{k})=\frac{E(\mathbf{k})-(\mathbf{k}+\mathbf{q})^2+\epsilon(\mathbf{k})}{\{c^2(\mathbf{k})+[E(\mathbf{k})-(\mathbf{k}+\mathbf{q})^2+\epsilon(\mathbf{k})]^2\}^{1/2}}, \tag{13}$$
$$A_2(\mathbf{k})=\frac{c(\mathbf{k})}{\{c^2(\mathbf{k})+[E(\mathbf{k})-(\mathbf{k}+\mathbf{q})^2+\epsilon(\mathbf{k})]^2\}^{1/2}},$$
$$E(\mathbf{k})=k^2+q^2-[(2\mathbf{k}\cdot\mathbf{q}-\epsilon(\mathbf{k}))^2+c^2(\mathbf{k})]^{1/2},$$
$$\sigma_z\alpha=\alpha,$$
$$\sigma_z\beta=-\beta,$$
$$\hbar=2m=1.$$

Used as trial functions in the Hartree-Fock equation, these eigenfunctions lead to a one-electron potential of the form of (12), and integral equations for the functions $c(\mathbf{k})$, $d(\mathbf{k})$, and $\epsilon(\mathbf{k})$. In particular,

$$c(\mathbf{k})=-\sum_{k'\text{ occupied}}V(\mathbf{k},\mathbf{k}')A_1(\mathbf{k}')A_2(\mathbf{k}'), \tag{14}$$

where $V(\mathbf{k},\mathbf{k}')$ is the $\mathbf{k}-\mathbf{k}'$ Fourier component of the electron-electron interaction. When we approximate $V(\mathbf{k},\mathbf{k}')$ by a constant, we may obtain c as the root of a transcendental equation. ϵ vanishes, and d becomes a constant having no effect on the physics. With this model of the interaction, the spin-density-wave configuration is no longer the ground state of the electron gas.[15] We shall work with this model nonetheless because of its greater simplicity. We shall discuss the

[15] A. W. Overhauser, Phys. Rev. 128, 1437 (1962).

probable effect of this assumption later, but it is clear even now that nothing important is lost thereby.

A second set of solutions to the Schrödinger equation with the potential (12), the upper-band states mentioned in the preceding section, are of similar form.

$$\psi_{\mathbf{k}}{}^{u}=[B_1 e^{i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}}\alpha+B_2 e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}}\beta](1/\sqrt{\Omega})e^{iE_u(\mathbf{k})t},$$
$$B_1=-A_2(\mathbf{k}),$$
$$B_2=A_1(\mathbf{k}), \tag{15}$$
$$E_u(\mathbf{k})=k^2+q^2+[(2\mathbf{k}\cdot\mathbf{q})^2+c^2(\mathbf{k})]^{1/2}.$$

To avoid obscuring the argument, we shall first carry out the discussion as if none of these states were occupied; relaxing this restriction will be easy.

We assume a form for the interaction of the electrons with the magnetized impurities,

$$\sum_{\mathbf{R}} V(\mathbf{r}-\mathbf{R})+J(\mathbf{r}-\mathbf{R})\bar{\sigma}\cdot\mathbf{S}_{\mathbf{R}}. \tag{16}$$

Various $\mathbf{R}$ refer to different scattering sites; $\mathbf{S}_{\mathbf{R}}$ is an angular momentum associated with each site. The axis of quantization is chosen to lie along the direction of the conduction-electron polarization at the site. This z direction is different from that in Eqs. (13) and (15). Since the interaction (16) involves the electron spin, we must express the electron-spin operators $\bar{\sigma}_z$, $\bar{\sigma}^+$, $\bar{\sigma}^-$ referred to the polarization axes in terms of those implied in Eqs. (13) and (15)

$$\bar{\sigma}_z=\sigma_x\cos 2\mathbf{q}\cdot\mathbf{R}+\sigma_y\sin 2\mathbf{q}\cdot\mathbf{R},$$
$$\bar{\sigma}^{\pm}=\sigma_z\pm i[\sigma_x\sin 2\mathbf{q}\cdot\mathbf{R}-\sigma_y\cos 2\mathbf{q}\cdot\mathbf{R}]. \tag{17}$$

Our unperturbed states of the combined electron-impurity system are Slater determinants of functions of the type Eqs. (13) and (15), multiplied by products of angular momentum wave functions oriented by the polarization. The states of differing $S_{z\mathbf{R}}$ are split by the diagonal elements of the interaction $J(0)\sum_{k\text{occ}}A_1(\mathbf{k})A_2(\mathbf{k})$, and we use the off-diagonal terms to calculate the scattering.

The scattering events which come from the spin-independent part of the interaction and the $\bar{\sigma}_z$ part of the spin-dependent term conserve the one-electron energy $E(\mathbf{k})$. The remaining part of the interaction, proportional to $\bar{\sigma}^+S^-$ or $\bar{\sigma}^-S^+$, flips the impurity and electron spin. Since the levels of the impurity spin are split by the interaction, the collisions caused by the flipping terms are inelastic from the point of view of the electrons alone.

The matrix elements of the scattering interaction will be proportional to certain Fourier components of the functions $V(\mathbf{r}-\mathbf{R})$ and $J(\mathbf{r}-\mathbf{R})$. We approximate these functions by constants. In systems where our assumption of localized impurities is valid, the errors introduced by this assumption will not be serious. Furthermore, in the ferromagnetic case where the transport problem may be solved without recourse to this approximation, the results may be compared and are found to be the same in all significant respects.[11] With this assumption, we may write $W(\mathbf{k},\mathbf{k}')$ as the sum of three terms.

$$W^0(\mathbf{k}'\mathbf{k})=\langle[V[A_1(\mathbf{k}')A_1(\mathbf{k})+A_2(\mathbf{k}')A_2(\mathbf{k})]+MJ[A_1(\mathbf{k}')A_1(\mathbf{k})-A_2(\mathbf{k}')A_2(\mathbf{k})]]^2\rangle_{\text{av}}(2\pi N/\Omega^2)\delta(E(\mathbf{k}')-E(\mathbf{k})),$$
$$W^+(\mathbf{k}'\mathbf{k})=\tfrac{1}{4}J^2(A_1'A_1-A_2'A_2+A_2A_1'-A_2'A_1)^2\langle(\mathcal{S}^+)^2\rangle_{\text{av}}(2\pi N/\Omega^2)\delta(E(\mathbf{k}')-E(\mathbf{k})+\Delta E), \tag{18}$$
$$W^-(\mathbf{k}'\mathbf{k})=\tfrac{1}{4}J^2(A_1'A_1-A_2'A_2+A_2'A_1-A_1'A_2)^2\langle(\mathcal{S}^-)^2\rangle_{\text{av}}(2\pi N/\Omega^2)\delta(E(\mathbf{k}')-E(\mathbf{k})-\Delta E),$$
$$(\mathcal{S}^{\pm})^2=S(S+1)-M(M+1),\quad M\equiv\mathcal{S}_z,$$
$$\Delta E\equiv\mu_K T=\text{Zeeman splitting}.$$

The angular brackets indicate a thermodynamic average over the Zeeman levels of the scattering centers. These expressions can be cast in a form which better illustrates the properties we shall use in finding the solution of the Boltzmann equation.

$$W^0(\mathbf{k}'\mathbf{k})=(\pi N/\Omega^2)\{V^2(1+\sin\phi\sin\phi'+\cos\phi\cos\phi')-2VJ\langle M\rangle_{\text{av}}(\sin\phi+\sin\phi')$$
$$+\langle M^2\rangle_{\text{av}}J^2(1+\sin\phi\sin\phi'-\cos\phi\cos\phi')\}\delta(E'-E),$$
$$W^{\pm}(\mathbf{k}'\mathbf{k})=(\pi N/2\Omega^2)J^2\langle(\mathcal{S}^{\pm})^2\rangle_{\text{av}}(1\mp\sin\phi)(1\pm\sin\phi')\delta(E'-E\pm\Delta E),$$
$$-e\mathcal{E}\cdot\nabla_k f_0=-(\Omega/8\pi^3)\int[W^0(k'k)(\Delta f-\Delta f')$$
$$+W^+(\mathbf{k}'\mathbf{k})(\Delta fQ(-x,\mu)-\Delta f'Q^{-1}(x,-\mu))+e^{\mu}W^-(\mathbf{k}'\mathbf{k})[\Delta fQ(x,\mu)-\Delta f'Q^{-1}(-x,-\mu)]]d\mathbf{k}', \tag{19}$$

where we have defined

$$\sin\phi_{\mathbf{k}}\equiv-2A_1(\mathbf{k})A_2(\mathbf{k}). \tag{20}$$

$\sin\phi_{\mathbf{k}}$ is an even function under inversion of the argument k and $\cos\phi_{\mathbf{k}}$ is odd. In this form, the Boltzmann equation is soluble, for Eq. (19) is an expression for Δf in terms of $\sin\phi$ and $\cos\phi$. Since the functional form of Δf is therefore

known, except possibly for constants determined by integrals of Δf, the integrals may all be performed and simple algebraic relations found for the unknown constants. It is at this stage that we have used our assumption about the constant Fourier coefficients of the interaction potentials, for this assumption gives the kernel in Eq. (19) the simple, degenerate form which permits the solution.

If we define $\Delta f \equiv \partial f_0/\partial E \nabla_k E \cdot \mathcal{E}\tau(\mathbf{k})$, we have for the electric current

$$I = (e\Omega/8\pi^3)\int_{-\zeta/\kappa T}^{\infty}\int_{S(E)} \tau(k)\frac{\mathcal{E}\cdot\nabla_k E \nabla_k E}{|\nabla_k E|}dS(E)\frac{\partial f_0}{\partial x}dx, \quad x \equiv [E(k)-\zeta]/\kappa T. \tag{21}$$

For electric fields normal to the direction of the spin-density-wave vector,

$$\tau_N = \frac{\Delta f}{\mathcal{E}\cdot\nabla_k E \partial f_0/\partial E} \equiv \frac{e}{g+h\sin\phi} = (e\Omega 8\pi^2/N)\{(V^2+\langle M^2\rangle_{\rm av}J^2)(P_5(E)+P_6(E)\sin\phi) - 2VJ\langle M\rangle_{\rm av}(P_6(E)-P_5(E)\sin\phi)$$
$$+\tfrac{1}{4}J^2\langle(S^+)^2\rangle_{\rm av}[(P_5(E-\Delta E)+P_6(E-\Delta E))(1-\sin\phi)Q(-x,\mu)$$
$$+(P_5(E+\Delta E)-P_6(E+\Delta E))(1+\sin\phi)Q(x,\mu)]\}^{-1}; \tag{22}$$

$$P_5(E) \equiv \int \delta(E-E(\mathbf{k}'))d\mathbf{k}', \quad P_6(E) \equiv \int \delta(E-E(\mathbf{k}'))\sin\phi' d\mathbf{k}'; \tag{23}$$

while if $\mathcal{E}$ and $\mathbf{q}$ are parallel,

$$\tau_P = \tau_N\left\{1+\frac{[\cos\phi/(c\cot\phi-2q^2\cos\phi)]\left[\frac{2\pi N}{\Omega}(V^2-\langle M^2\rangle_{\rm av}J^2)\int_{S(Ek)}\cos\phi'\tau_N(\phi')[c\cot\phi'-2q^2\cos\phi']dS\right]}{e-(\pi N/\Omega)(V^2-\langle M^2\rangle_{\rm av}J^2)\int_{S(Ek)}\tau_N(\phi')\cos^2\phi' dS}\right\}. \tag{24}$$

To include the effect of the states of the upper band, the integrals of Eqs. (21) through (24) are extended over the upper-band sheet of the Fermi surface. The corresponding expressions for the excess heat current are different only in the appearance of an additional factor x in the integrand. In the curves that follow, the functions $P_5(E\pm\Delta E)$ and $P_6(E\pm\Delta E)$ have been approximated by their values at the Fermi surface, since they are quite slowly varying. The effect of this final approximation is the failure of the ordinary thermoelectric effect to appear.[11]

RESULTS

The resistivity and the thermoelectric power were evaluated from the expressions of the preceding section for selected values of the parameters. We first examined the thermoelectric power as a function of temperature for a spin-density-wave vector magnitude equal to the Fermi diameter, for the Hartree-Fock theory of the free-electron gas predicts a spin-density-wave instability at about this wavelength. In Fig. 3 we show some typical results.

The temperature is measured in units of $\Delta E/\kappa$, the thermopower in κ/e; for a fractional polarization of 8% and $J=0.03$ eV, $T=1$ corresponds to 29°K. The magnitude of q is that appropriate for an electron density of 10^{23} cm^{-3}. The amplitude of the spin-density wave has been chosen so that the fractional polarization of the electron gas is 0.08.

These curves share some features of the experimental

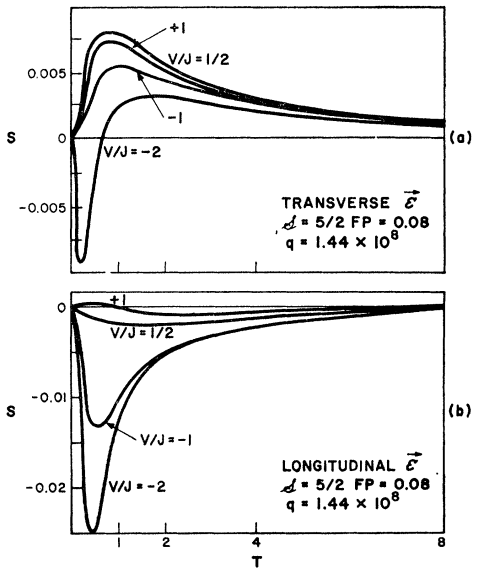

FIG. 3. Thermoelectric power as a function of temperature for a single short-wavelength spin-density-wave electron gas. "Longitudinal" and "transverse" describe the orientation of the electric field with respect to the spin-density-wave vector. The thermoelectric power is expressed in units of $(\kappa/e)=86.3$ μV/deg; the temperature in units of (Zeeman splitting)/κ.

dilute alloys results in that they show a sharp rise or drop from zero at the lowest temperatures, reach a maximum and then decay. In Fig. 3, however, the magnitude of the effect is still too small by at least a factor 10 in comparison with the experiments. Also, the effect with **E** transverse to **q** has the wrong sign.

We may replace the constant c in our equations by a function of wave vector which diminishes for **k** far from the energy gap. Constant c is the condition obtaining when the electron-electron interaction matrix element is assumed a constant. The diminishing $c(\mathbf{k})$ should provide a better approximation to the behavior of an electron gas less effectively screened than the constant matrix element implies. In this "unscreened" model, the spiraling electron polarization drops more abruptly as a function of displacement of **k** from the gap. The division of the electrons into two scattering groups is thereby sharpened.

In Fig. 4 we see the effect of this modification on the thermoelectric power. The increase is not great enough to bring the theory in line with the experiments.

The expected fall off in c as a function of **k** allows us to consider linear spin density waves, for when the energy gaps associated with two spirals of different **q** are widely separated in k space, we may regard the two spirals as essentially noninteracting and approximate the electron wave functions with those appropriate to the energy gap nearest. When the wave vectors of two spin-density waves are equal and opposite, then the net electron polarization as probed by localized moments is homogeneous in direction and varies sinusoidally in magnitude. When the wave vector **q** is small, however, the strongly perturbed regions in k space are near one another, and the interaction between the two spirals must be considered, making the problem much more difficult.

The scattering behavior is quite different in the linear and spiral cases. With a linear spin-density wave, the impurity spins do not all see the same internal field, as in the spiral. Hence scattering off different ions involves different inelasticities. As a function of temperature we may therefore expect to see the features of the transport coefficients broadened and shifted in the low-temperature direction. The spatially varying components of the electron spins still spiral; the ion spins, aligned by the total electron polarization, are quantized along a fixed direction. Therefore, except where the polarization directions of the two contributing spirals are coincident, the strongly polarized electrons do not line up with the spin of the ion from which they are scattered, in contrast to the single spiral case. This weakens the one-wayness of the scattering, for it is now possible for an electron at a gap to scatter by flipping an ion spin up, losing energy in the process, a type of event forbidden with a single spiral. We expect a reduced thermoelectric anomaly.

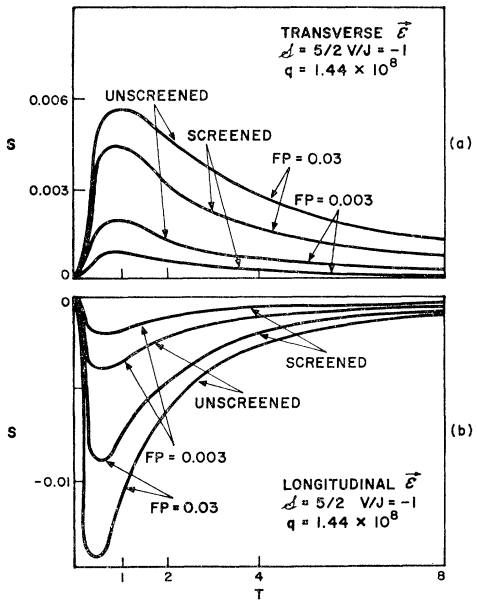

FIG. 4. Thermoelectric power as a function of temperature for screened and unscreened models of the electron gas. The parameters have been adjusted so that the fractional antiferromagnetic polarization of the electron gas, and hence the temperature scales, will be comparable in the two models.

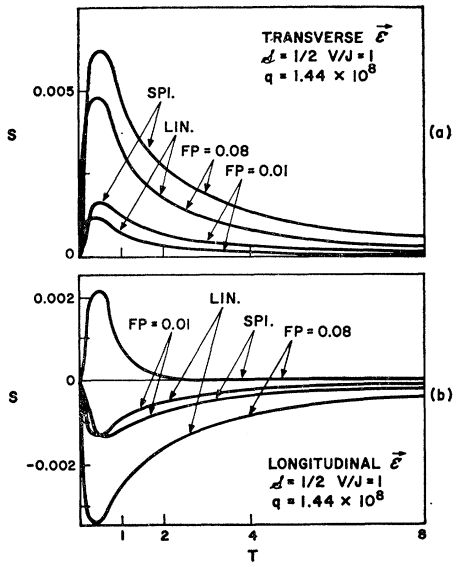

FIG. 5. Thermoelectric power versus temperature for single and double spiral-spin-density waves, spiral and linear SDW's, respectively. The maximum Zeeman splitting in the linear model equals the splitting for the spiraling case.

Figure 5 contrasts the thermoelectric-power calculation for the linear and spiral cases. The parameters have been adjusted so that the total electron polarization is the same fraction in both cases. The use of an unreasonably small ion spin ($S=\frac{1}{2}$), to simplify some of the intermediate calculations has reduced the effect.

Also, the modification of the wave functions unperturbed by the first spiral by the introduction of the second spiral has profoundly affected the longitudinal effect.

The temperature behavior of the resistivity for the cases of Fig. 5 is shown in Fig. 6. These curves are interesting because, together with a phonon contribution, they show a resistivity minimum followed by a maximum. We regard them as a curiosity, however,

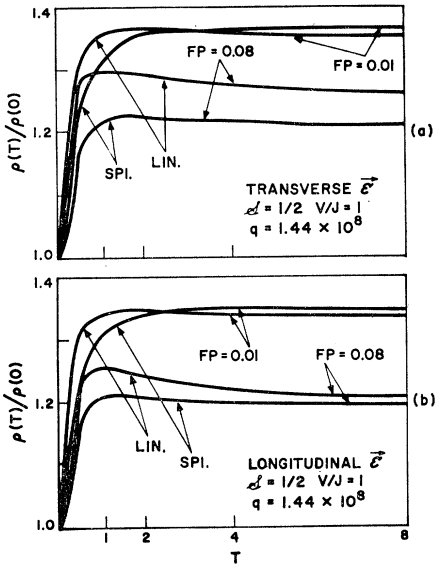

FIG. 6. Resistivity as a function of temperature, measured relative to the resistivity at 0 deg for the linear and spiral models. For $V/J<0$, the maxima disappear.

rather than as an important result. Relative to the peak in the thermoelectric effect, the resistivity maxima of Fig. 6 come at too high a temperature. Furthermore, the sign of V/J is opposite both to what it is usually assumed to be and to that which is necessary to obtain the correct sign of the thermopower (Fig. 7)[16]; the interesting features of Fig. 6 do not survive the sign change.

[16] Cf., Eq. (16).

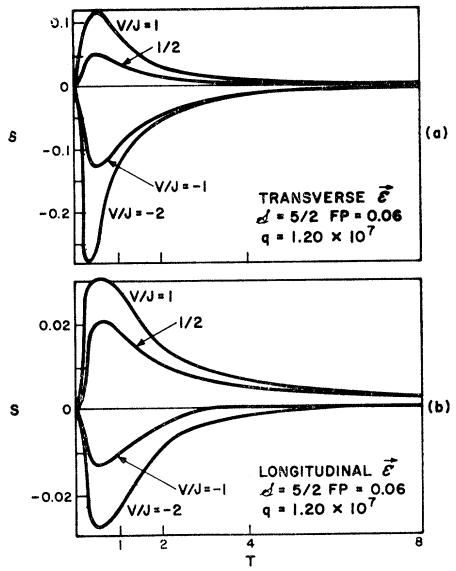

FIG. 7. Thermoelectric power versus temperature for a long-wavelength, spiral spin-density-wave model. The maximum magnitude of S in 7a is approximately 23 μV/deg.

Figure 7 shows the thermoelectric power calculated for a spin-density wave vector less than one-tenth the Fermi radius. The dramatic increase in the effect is due to the substantial population of states of the upper band. We notice that the thermoelectric power has the same sign as V/J; this feature is shared by the Kasuya model. The maximum magnitude of the thermopower in these curves is a little over 23 μV/deg.

We have already remarked on the Hartree-Fock instability which might lead to a **q** vector spanning the Fermi surface. The narrow necks where the Fermi surfaces of the noble metals make contact with the Brillouin-zone edges could be spanned by a **q** vector of the size necessary to produce Fig. 7.

We conclude that the spin-density-wave hypothesis can lead to large thermoelectric anomalies in a paramagnetic alloy. However, a consistent interpretation of observed transport anomalies on this basis does not appear easy, if at all possible.