Magnetic Susceptibility of a Simple Charge-Density-Wave Metal

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(Received 27 August 1979)

The total magnetic susceptibility of the conduction electrons is calculated for a simple metal containing a charge-density wave. A large (~18%) anisotropy in the susceptibility is predicted for the charge-density wave model of potassium. In this case, the susceptibility is most paramagnetic when the magnetic field and charge-density wave vector, $\vec{Q}$, are parallel. The possibility of producing single-$\vec{Q}$ samples by cooling in a magnetic field is discussed.

The purpose of this paper is to calculate the magnetic susceptibility of the conduction electrons in a simple metal containing a charge-density wave (CDW). In particular, the "simple metal" chosen for discussion is the CDW model of potassium. The experimental evidence supporting the existence of a CDW ground state in potassium has recently been reviewed by Overhauser.[1] The effects of electron-electron interactions are not included in this work.

As shown below, if potassium contains a CDW, the conduction-electron susceptibility has a large (~18%) anisotropy. The susceptibility is most paramagnetic when the magnetic field $\vec{H}$ is parallel to the CDW vector $\vec{Q}$. The anisotropic part of the susceptibility depends on the square of the sine of the angle between $\vec{H}$ and $\vec{Q}$. Experimental consequences of this anisotropy will be discussed below.

Only the bare essentials of the CDW model of potassium needed for the calculation are included here. Additional detail can be found in the review by Overhauser[1] and references therein. In the presence of a CDW, each electron experiences a sinusoidal potential

$$V = G\cos\vec{Q}\cdot\vec{r}, \tag{1}$$

where G is the CDW energy gap and $\vec{Q}$ is the CDW vector. Thus, a metal which is isotropic (cubic) in the absence of the CDW acquires an anisotropy characterized by the direction of $\vec{Q}$. The assumption that the CDW ground state of potassium is described by a single plane-wave component (in contrast to the transition metal dichalcogenides, for example, which exhibit CDW phases described by three $\vec{Q}$'s) follows from experiment. Bishop and Overhauser[2] have shown that the twofold anisotropy of the residual resistivity of potassium deduced from the induced-torque measurements of Holroyd and Datars[3] demonstrates the uniaxial nature of the CDW distortion.

The CDW potential perturbs the one-electron wave functions and energies (which are taken as those of free electrons in the absence of the CDW), causes energy gaps at $\vec{k} = \pm Q/2$, and leads to a modified Fermi surface. For this paper the Fermi surface is taken to be that which touches the energy gaps at a point, i.e., the case of critical contact.[4] A simple and often useful feature of this model is that integrations over d^3k can be replaced by the equivalent expression

$$d^3k = (m/\hbar^2)dE\,d\Phi\,dk_z, \tag{2}$$

where E is the electron energy and the choice of cylindrical coordinates with $\hat{z}$ parallel to $\vec{Q}$ has been made.

Use of (2) makes calculation of the Pauli susceptibility trivial with the result

$$\chi_p = \frac{3}{2}\mu_B{}^2\left(\frac{n}{\epsilon_F}\right)\left(\frac{Q}{2k_F}\right) \equiv \chi_0\left(\frac{Q}{2k_F}\right), \tag{3}$$

where n is the number of electrons per unit volume, and k_F and ϵ_F are the radius and energy of the unperturbed Fermi sphere, respectively. χ_0 is the free-electron Pauli susceptibility. The factor $Q/2k_F$ reflects the higher density of states at the Fermi surface when a CDW is present.

The theory of the diamagnetic susceptibility of conduction electrons has been studied extensively. It is convenient to use the results of Misra and Roth[5] for the diamagnetic susceptibility. They treat the case of nearly free electrons and, specifically, consider the case when electrons are near the energy gaps. References to additional work on the subject may be found in the Misra and Roth paper.

A useful starting point for calculating the orbital contribution to the susceptibility is Eq. (6.6) of Misra and Roth modified for the present notation.[6] For simplicity, choose coordinate axes such that

$\vec{\mathrm{H}} = H\hat{z}\cos\theta + H\hat{x}\sin\theta$ and $\vec{\mathrm{Q}} = Q\hat{z}$. Then

$$\chi_{\mathrm{orb}} = \frac{{\mu_{\mathrm{B}}}^2}{12\pi^3}\int d^3k\, f'(E) + \frac{4{\mu_{\mathrm{B}}}^2 m^2 Q^2 \sin^2\theta}{\pi^3\hbar^4}\left\{\int d^3k\, f'(E)\frac{G^2}{[(Q^2+2k_zQ)^2+g^2]^{3/2}}\left[\frac{1}{6}-\frac{{k_y}^2}{[(Q^2+2k_zQ)^2+g^2]^{1/2}}\right] + \frac{m}{\hbar^2}\int d^3k\, f(E)\frac{G^2}{[(Q^2+2k_zQ)^2+g^2]^2}\left[1+\frac{8{k_y}^2}{[(Q^2+2k_zQ)^2+g^2]^{1/2}}\right]\right\}. \tag{4}$$

$f(E)$ is the Fermi occupation factor, $f'(E) \equiv df(E)/dE$, and $g \equiv 2mG/\hbar^2$. A factor of 2 has been included to account for the two energy gaps.

It is convenient to label the five terms on the right-hand side of Eq. (4) as χ_1 through χ_5. Let $\alpha = mG/\hbar^2Q^2$. The result to order α^2 is

$$\chi_1 = -\frac{1}{3}\chi_0\left(\frac{Q}{2k_{\mathrm{F}}}\right), \quad \chi_2 = -\frac{1}{3}\chi_0\left(\frac{Q}{2k_{\mathrm{F}}}\right)\left(1-\frac{1}{2}\alpha^2\right)\sin^2\theta, \quad \chi_3 = \chi_4 = \frac{1}{2}\chi_0\left(\frac{Q}{2k_{\mathrm{F}}}\right)\left(1-\frac{\pi}{4}-\frac{\pi}{4}\alpha+\frac{1}{2}\alpha^2\right)\sin^2\theta,$$
$$\chi_5 = \frac{1}{2}\chi_0\left(\frac{Q}{2k_{\mathrm{F}}}\right)\left\{\frac{5}{3}-\frac{\pi}{2}+\alpha\left(\frac{2}{3}-\frac{\pi}{2}\right)+\alpha^2\left[\frac{1}{6}+\ln\left(\frac{1+(1+\alpha^2)^{1/2}}{\alpha}\right)\right]\right\}\sin^2\theta. \tag{5}$$

χ_1 is the usual result for the Landau diamagnetism of free electrons modified by the factor $Q/2k_{\mathrm{F}}$ which represents the increased density of states at the Fermi surface (as above for the Pauli susceptibility). Note that the "anisotropy" terms, χ_2 through χ_5, are independent of the CDW energy gap G to lowest order although the value of the leading term depends on the geometry of the Fermi surface near the gaps. The dependence of the leading term in χ_2 through χ_5 on Fermi-surface geometry near the gaps is not too strong for the large CDW energy gaps [$G \simeq 0.6$ eV (Ref. 1)] of interest here. The values above were calculated for a Fermi surface in critical contact with the energy gaps but are essentially unchanged if the Fermi surface misses the energy gaps only slightly (on a scale set by G) or contacts the energy gaps in small necks.

Although there would be no way to turn off the CDW at zero temperature it is interesting to examine the limit of the orbital susceptibility as $G \to 0$. That the leading terms in χ_2 through χ_5 are explicitly independent of G means that this must be done with care. It is possible to show for a Fermi surface which does not contact the energy gaps that the coefficient of the α^0 term vanishes as $G \to 0$ since the number of strongly perturbed states shrinks to zero rapidly enough. Moreover, for a Fermi surface which contacts the energy gaps with finite area, states above the gap will be occupied as $G \to 0$ (since the unperturbed Fermi surface is spherical); and the α^0 term goes to zero because of a cancellation of states above and below the gap. For the case of critical contact, the α^0 term does not vanish as $G \to 0$. Although the number of strongly perturbed states decreases as $G \to 0$, the contribution to χ from each state grows in inverse proportion. That critical contact gives an unphysical result in this case is not surprising since the Fermi surface near the gaps is changed from a smooth, curved surface to a cone for any $G > 0$. Of course, as stated above, this is not a problem for the large G of interest here.

The value of G proposed for potassium is $G \cong 0.6$ eV.[1] With use of this value the total susceptibility is

$$\chi \cong \frac{2}{3}\chi_0\left(\frac{Q}{2k_{\mathrm{F}}}\right) - (0.11)\chi_0\left(\frac{Q}{2k_{\mathrm{F}}}\right)\sin^2\theta. \tag{6}$$

If χ_{avg} is the solid-angle average of χ and the anisotropy is defined as

$$\eta = (\chi_{\max} - \chi_{\min})/\chi_{\mathrm{avg}}, \tag{7}$$

then $\eta = 0.185$. For $G = 0.6$ eV and critical contact, $Q/2k_{\mathrm{F}} \cong 1.06$.

The relatively large effect calculated here is atypical of the size of band-structure effects on the susceptibilities of simple metals. Typically, band structure produces a ~ (2 to 5)% change in the diamagnetic susceptibility from its free-electron value.[5] This occurs in monovalent metals because the Fermi surface is not too close to the energy gaps. In polyvalent metals cancellations occur for electrons below and above the gaps. Moreover, the effect described here is anisotropic in contrast with the isotropic effects of the crystal potential in cubic metals.

The large anisotropy in the susceptibility gives rise to a number of interesting experimental possibilities. Before discussing the most important of these it is necessary to review the concept of $\vec{Q}$ domains. In a (single crystal) sample $\vec{Q}$ will point along a specific crystallographic direction. Because there are a number of equivalent directions,[7] it is possible to have a domain structure with $\vec{Q}$ pointing in different (equivalent) directions in different parts of the (single) crystal. Stress is thought to be very important in determining this preferred local direction of $\vec{Q}$.[1] A "well-characterized" sample is one with a single $\vec{Q}$ domain throughout. Multiple-$\vec{Q}$-domain samples would lead to sample-dependent results in many types of experiments.[1]

If a single-$\vec{Q}$ sample of potassium can be obtained, then a measurement of the total susceptibility as a function of sample orientation will offer evidence of the presence of a CDW. Obtaining a single-$\vec{Q}$ sample is not an easy task. Such a sample was grown by Holroyd and Datars inside a spherical Kel-F mold.[1,3] This sample exhibited a giant anisotropy in induced-torque experiments.[3] Bishop and Overhauser have discussed this point in more detail.[2]

It was mentioned above that stress appears to play an important role in $\vec{Q}$-domain orientation. Because of the susceptibility anisotropy discussed here, an applied magnetic field should also influence $\vec{Q}$-domain orientation.[8] Suppose that a molten sample of potassium is cooled in a magnetic field. Since χ is most paramagnetic when $\vec{Q}$ is parallel to $\vec{H}$, the (possible, crystallographic) direction of $\vec{Q}$ which is most nearly parallel to $\vec{H}$ will be preferred as the sample crystallizes. Since there is no quantitative theory of the stress effects involved in orienting $\vec{Q}$, it is not possible at this time to estimate the size of the magnetic field necessary to produce a single-$\vec{Q}$ sample. If such a technique should prove successful, single-$\vec{Q}$ samples could effectively be "mass produced" and subjected to a variety of experimental techniques such as the de Haas–van Alphen effect, induced-torque measurements, helicon resonance, etc. Indeed, an interesting possibility would be to measure the susceptibility of a field-cooled sample. A simple method for $\vec{Q}$-domain control would, as emphasized by Overhauser,[1] be the bane of sample dependence and irreproducibility which has marked the history of research on potassium.

Support by the National Science Foundation and the Cornell Materials Science Center under Contract No. DMR-76-81083 A02 and Technical Report No. 4183 is gratefully acknowledged.

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[5] P. K. Misra and L. M. Roth, Phys. Rev. 177, 1089 (1969).

[6] The first two signs in Eqs. (6.6) of Misra and Roth are in error as printed and have been corrected here. The errors appear only in this one equation.

[7] Recent theoretical work indicates there are likely to be 24 equivalent directions; G. Giuliani and A. W. Overhauser, Phys. Rev. B 20, 1328 (1979).

[8] Single spin-density-wave domain samples of chromium have been produced by field cooling. R. A. Montalvo and J. A. Marcus, Phys. Rev. Lett. 8, 151 (1964); A. Arrott, S. A. Werner, and H. Kendrick, Phys. Rev. Lett. 14, 321 (1965).