Phason narrowing of the nuclear magnetic resonance in potassium

Y. R. Wang and A. W. Overhauser
Department of Physics, Purdue University, West Lafayette, Indiana 47907
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Nuclear magnetic resonance in a metal having an incommensurate charge-density wave (CDW) should exhibit significant broadening because the Knight shift depends on the conduction-electron density surrounding each nucleus. Nevertheless, experiments on metallic potassium at 1.5 K have not revealed such an effect. Thermal excitation of phasons, the low-frequency collective modes of a CDW, cause sufficient motional narrowing to explain this observation. However below 100 mK, as the CDW phase excitations subside, the NMR line should broaden rapidly with decreasing temperature.

I. INTRODUCTION

Charge-density-wave (CDW) instabilities in simple metals are caused by the many-body effects of exchange and correlation.[1] The conduction electrons have lower energy if they have a sinusoidally modulated charge density,

$$\rho(\mathbf{r})=\rho_0[1+p\cos(\mathbf{Q}\cdot\mathbf{r}+\phi)]\,, \tag{1}$$

rather than a uniform value ρ_0. The CDW wave vector is approximately[2]

$$Q\approx 2k_F(1+G/4E_F)\,, \tag{2}$$

where G is the CDW energy gap, and k_F and E_F are the Fermi-surface radius and energy. For an alkali metal the direct of $\mathbf{Q}$ is tilted a few degrees away from a $\langle 110\rangle$ axis.[3] The CDW amplitude p, in the case of potassium, is ~ 0.11.[4] Since the broken symmetry is incommensurate with the lattice, the total electronic energy is independent of the phase ϕ,

A wealth of experimental evidence[5] has shown the effects of the CDW's in Na and K. The most dramatic example to date is the direct observation of open orbits in high magnetic fields.[6] These orbits arise from higher-order energy gaps, which truncate the Fermi surface.[7] Induced-torque anisotropies[8] below 3 T have also shown that the Fermi surface is multiply connected and lacks cubic symmetry.[5] Both the open-orbit spectra[9] and the induced-torque anisotropy[10] have been explained. These phenomena contradict the simple interpretation of de Haas—van Alphen experiments,[11] which suggest a simply connected and isotropic Fermi surface. In light of the open-orbit observations, the most reasonable understanding[12] of de Haas—van Alphen isotropy is that published data have been obtained on samples with a very small Q-domain size.[13]

A significant theoretical problem[14] which needs study concerns the nuclear-magnetic-resonance (NMR) linewidth in potassium. The CDW broken symmetry will lead to an extremely broadened NMR signal—much larger than the Van Vleck dipolar width,[15] ~ 0.14 G. There are two major sources of additional broadening: quadrupole perturbations and Knight-shift variations.

A CDW in a cubic metal leads to quadrupole broadening because the positive-ion lattice sustains a periodic lattice displacement,[1]

$$\mathbf{u}(\mathbf{r})=\mathbf{A}\sin(\mathbf{Q}\cdot\mathbf{r}+\phi)\,, \tag{3}$$

in order to compensate the charge modulation of the conduction electrons. The displacement amplitude has a magnitude,[4]

$$A\approx\frac{p}{Qf(Q)}\sim 0.03\ \text{Å}\,, \tag{4}$$

where $f(Q)$ is the total-charge form factor of the positive ion for wave-vector Q. ($f\sim 2.9$ rather than unity.) An analysis of quadrupole effects has already been presented in detail,[16] but a value $A\sim 0.11$ Å was assumed. The value (4) will considerably reduce the estimated quadrupole broadening. Therefore, the present work will focus on the dominant source of CDW broadening: Knight-shift variations.

We shall find that at $T=0$ K and $H_0=6$ T the NMR linewidth caused by Knight-shift variations (from the crests to the troughs of the CDW) is ~ 34 Oe, a value more than 2 orders of magnitude larger than the observed width,[16] 0.27 Oe, at $T=1.5$ K. The main thrust of this paper is to show that thermal excitation of phasons,[17] the low-frequency collective modes of an incommensurate CDW, provide sufficient motional narrowing[18] to explain the experimental result at $T=1.5$ K, the lowest temperature studied so far. The emphasis will be on the temperature dependence of the phason narrowing. Below about 100 mK the effect of the CDW structure should become apparent, and the NMR line should broaden rapidly as T is further reduced.

II. NMR LINE SHAPE AT $T=0$ K

The Knight shift K_0 is defined by the NMR frequency shift in a metal,[19]

$$\omega\equiv\omega_d(1+K_0)\,, \tag{5}$$

relative to the frequency ω_d in a diamagnetic salt. The shift arises from the spin paramagnetism of the conduc-

tion electrons. For potassium, $K_0=0.26\%$.[20] If potassium were truly body-centered cubic (no CDW) each nuclear spin would, for $H_0=6$ T, experience a hyperfine field of 156 Oe. However, the Knight shift in a CDW state will depend on position in a way similar to the local electron density, Eq. (1):

$$K(\mathbf{r})=K_0+\kappa\cos(\mathbf{Q}\cdot\mathbf{r}+\phi)\ . \tag{6}$$

It is a simple exercise to show that the probability distribution $P(\Delta K)$ for a given Knight shift $K_0+\Delta K$ is

$$P(\Delta K)=\frac{1}{\pi[\kappa^2-(\Delta K)^2]^{1/2}}\ . \tag{7}$$

This distribution is shown in Fig. 1 and has singularities at the limits $\pm\kappa$. This figure would describe the expected NMR line shape if the CDW phase ϕ did not fluctuate. Analogous line shapes for metals with two or three CDW's have been calculated.[21] In potassium the anisotropy of the CDW-induced optical absorption indicates that there is only one.[22]

In order to calibrate the width of the NMR line shape shown in Fig. 1 it is necessary to determine the parameter κ. It is a reasonable approximation to take

$$\kappa\approx pK_0\ , \tag{8}$$

where p is the fractional-charge modulation, Eq. (1). This modulation is caused by the exchange and correlation potential of the CDW:

$$V_{\rm CDW}(x)=G\cos(Qx)\ . \tag{9}$$

(We have chosen the $\mathbf{Q}$ direction along $\hat{\mathbf{x}}$.) The CDW gap for potassium is known[2] directly from optical-absorption data;[23] $G=0.62$ eV. A simple calculation of p from Eqs. (9) and (2) leads to an incorrect value of 0.17. The reason is that $V_{\rm CDW}$ is nonlocal; it arises entirely from exchange and correlation. The matrix elements of (9) are wave-vector dependent:

$$\begin{aligned}\langle k_x+Q\mid V_{\rm CDW}\mid k_x\rangle&\equiv\tfrac{1}{2}G_+(k_x)\ ,\\ \langle k_x-Q\mid V_{\rm CDW}\mid k_x\rangle&\equiv\tfrac{1}{2}G_-(k_x)\ .\end{aligned} \tag{10}$$

The nonlocal theory[24] of the G_+ and G_- has been fitted numerically:[25]

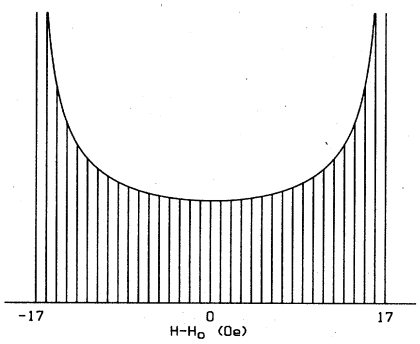

FIG. 1. NMR line shape at $T=0$ caused by a CDW in potassium. $H_0=6$ T.

$$G^+(k_x)\cong G/(1+2.2\mu-0.48\mu^2)\ , \tag{11}$$

where

$$\mu\equiv(k_x/Q)+\tfrac{1}{2}\ . \tag{12}$$

The fact that the CDW potential, Eq. (9), depends on the *axis* of $\mathbf{Q}$, and not on the vector direction, leads to a relation between G^+ and G^-:

$$G^-(k_x)=G^+(-k_x)\ . \tag{13}$$

Each conduction-electron wave function becomes amplitude modulated when the CDW perturbation (9) is included in Schrödinger's equation. Use of the nonlocal matrix elements (10) leads to[4]

$$p\approx 0.11\ . \tag{14}$$

This value implies, from Eq. (8), that the total CDW width of the NMR line is (for $H_0=6$ T)

$$2\kappa H_0\approx 34\text{ Oe}\ . \tag{15}$$

It must be emphasized that this value is an approximate one because Eq. (8) is not strictly correct. The charge modulation p corresponds to the Fermi-volume average of the wave-function amplitude modulation. The inhomogeneous Knight shift depends, instead, on the Fermi-surface density-of-states average p' of the wave-function modulation. However, the difference between p' and p is comparable to the uncertainty in p, Eq. (14), so we shall ignore the distinction.

The NMR line shape described above will be slightly narrowed (a few percent) by zero-point phase fluctuations. The theory of this effect[21] was presented several years ago, before the phason excitation spectrum for potassium was known; and this uncertainty led to an overestimate of the narrowing at $T=0$ K. We now turn to the motional narrowing caused by thermal excitation of phasons.

III. REVIEW OF PHASON PROPERTIES

Phasons are the low-frequency collective modes of a CDW broken symmetry.[17] The phase ϕ appearing in Eq. (1) becomes a dynamic variable. It can be expanded as follows:

$$\phi(\mathbf{r},t)=\sum_{\mathbf{q}}\phi_q\sin(\mathbf{q}\cdot\mathbf{r}-\omega_{\mathbf{q}}t+\gamma_{\mathbf{q}})\ , \tag{16}$$

where $\mathbf{q}$ and $\omega_{\mathbf{q}}$ are the phason wave vector and frequency. $\gamma_{\mathbf{q}}$, the phase of the phason, is randomly distributed between 0 and 2π. Phasons have a finite lifetime $\tau_{\mathbf{q}}$, which we discuss below. The randomness of $\gamma_{\mathbf{q}}$ arises from this fact together with the *assumption* that the CDW is not pinned by lattice imperfections.

The phason spectrum has a linear dispersion relation (for most of its range) and is anisotropic.[17] Suppose we take $\mathbf{Q}$ along $\hat{\mathbf{x}}$. Then,

$$\omega_{\mathbf{q}}\cong c_0(q_y^2+q_z^2+\gamma^2q_x^2)^{1/2}\ . \tag{17}$$

c_0 is the velocity of a phason traveling transverse to $\mathbf{Q}$, and γc_0 is the velocity parallel to $\mathbf{Q}$. The phason spectrum extends only to a cutoff frequency ω_ϕ.[26] The allowed $\mathbf{q}$'s lie in a small ellipsoidal volume of $\mathbf{q}$ space.

The three phason-spectrum parameters rae known approximately for potassium:

$$c_0 \approx 1.4\times 10^5 \text{ cm/sec} ,$$
$$\gamma \approx 8 , \tag{18}$$
$$\hbar\omega_\phi \approx 3 \text{ K} .$$

The estimate for c_0 is theoretical,[27] whereas γ and ω_ϕ are based on an analysis of phason contributions to the low-temperature electrical resistivity.[28] A theory of the point-contact spectrum in potassium,[29] for which experiments show an anomaly caused by electron-phason interactions, gives excellent agreement with use of the parameter set (18).

Another crucial quantity is the phason lifetime τ_q. The theory[30] is based on electronic excitations (from below to above E_F) caused by the electron-phason interaction. The result obtained is

$$\frac{1}{\tau_q} = \frac{\hbar Q^2 q}{32\pi n M A^2}\left[\frac{G}{4E_F}\right]\cos^2\theta , \tag{19}$$

where θ is the angle between $\mathbf{q}$ and $\mathbf{Q}$, n is the electron concentration, M the ionic mass, and A the CDW displacement amplitude, Eq. (4). G is the CDW energy gap (0.62 eV in potassium). Since Eq. (19) is proportional to q, the quality factor $\omega_q\tau_q$ for phasons is independent of $|\mathbf{q}|$. For potassium, Eq. (19) leads to a quality factor

$$\mu \equiv \omega_q\tau_q = \mu_0/\cos^2\theta , \tag{20}$$

with $\mu_0 \sim 4$. Another consequence of Eq. (19) is that $\tau_q \to \infty$ as $q \to 0$. This would imply that a sliding CDW would not experience a frictional force. Such a frictional force, in fact, arises from scattering processes responsible for the electrical resistivity.[31] This mechanism will also contribute to phason damping (but we neglect it here).

We emphasize that the anisotropies of the phason velocity and damping given by Eqs. (17) and (19) have not yet been adequately tested. In particular, the theory that leads to Eq. (19) is based on an electron-lattice interaction for which only longitudinal phonons can scatter electrons. Therefore, the anisotropies (especially for τ_q) discussed above are possibly exaggerated.

In the following section we will find that motional narrowing of the NMR line depends sensitively on the phason anisotropies. Accordingly, we will carry out several calculations depending on whether (or not) anisotropies of ω_q and τ_q are included.

IV. MOTIONAL NARROWING BY PHASONS

We will employ the theory of Pines and Slichter,[18] which determines the resonance width $1/T_2$ caused by frequency shifts $\pm w$ which (on average) continue for a correlation time τ_c. It is assumed that $w\tau_c \ll 1$. The resonance width is the reciprocal of the time it takes for the phase of the transverse magnetization to "diffuse" one radian. The number of steps N for such a random walk, having phase jumps $\pm w\tau_c$, is given by

$$N^{1/2}(w\tau_c) = 1 . \tag{21}$$

Since $T_2 = N\tau_c$, it follows (on eliminating N) that

$$\frac{1}{T_2} = w^2\tau_c . \tag{22}$$

The intrinsic width w is narrowed by the factor $w\tau_c$.

The only difference for the case of phason narrowing is that each phason mode contributes individually to the random walk. Consider a single term of Eq (16). The CDW phase change caused by such a mode between $t=0$ and $t=t$ is, at $\mathbf{r}=0$,

$$\Delta\Phi_q = \phi_q[\sin(-\omega_q t+\gamma_q) - \sin\gamma_q] . \tag{23}$$

The square of this change must be averaged over the random phase γ_q and over the distribution of phason lifetimes for that mode:

$$P(t) = \frac{1}{\tau_q}\exp\left[\frac{-t}{\tau_q}\right] . \tag{24}$$

The integrations are elementary. For an average lifetime τ_q

$$(\Delta\Phi_q)^2_{\text{av}} = \frac{\omega_q^2\tau_q^2}{1+\omega_q^2\tau_q^2}\phi_q^2 . \tag{25}$$

The correlation time τ_c will be (approximately) the time for the CDW phase at the point $\mathbf{r}=0$ to change by one radian as a consequence of the thermal excitation of *all* phason modes. Thus

$$\sum_q \frac{\tau_c}{\tau_q}(\Delta\Phi_q)^2_{\text{av}} \approx 1 . \tag{26}$$

The 1 in the denominator of Eq. (25) may be dropped, because of (20), so

$$\frac{1}{\tau_c} \approx \sum_q \frac{1}{\tau_q}\langle\phi_q^2\rangle , \tag{27}$$

where the angular brackets around ϕ_q^2 indicate the thermal-equilibrium average. Since the kinetic energy of a phason mode (normalized in unit volume) is[32]

$$T_q = \tfrac{1}{8}nMA^2\omega_q^2\phi_q^2 , \tag{28}$$

and since the mean thermal energy of a mode is

$$2\langle T_q\rangle = \hbar\omega_q[\exp(\hbar\omega_q/k_BT)-1]^{-1} , \tag{29}$$

we obtain

$$\langle\phi_q^2\rangle = \frac{4\hbar}{nMA^2\omega_q}[\exp(\hbar\omega_q/k_BT)-1]^{-1} . \tag{30}$$

Equations (27) and (30) determine the correlation time. Integration over the ellipsoidal $\mathbf{q}$ space of the phason spectrum leads to

$$\tau_c = \frac{\pi^2 nM\hbar^2A^2c_0^3}{k_B^3T^3DF(\Theta/T)} . \tag{31}$$

k_B is Boltzmann's constant, Θ is the phason cutoff frequency (~ 3 K), and

$$F(\Theta/T) \equiv \int_0^{\Theta/T}\frac{x^2\,dx}{\exp(x)-1} . \tag{32}$$

D is a numerical factor which depends on the anisotropies of the phason velocity and damping:

$$D \equiv \int_0^{\pi} d\theta \frac{\sin\theta}{\mu(\theta)(\sin^2\theta+\lambda^2\cos^2\theta)^{3/2}} . \quad (33)$$

λ and μ are defined by Eqs. (17) and (20).

We have already mentioned that the anisotropies which affect the value of D are not well established. So we shall evaluate D for four models (with $\mu_0=4$).

(a) Isotropic velocity ($\lambda=1$) and isotropic damping ($\mu=\mu_0$): $D=0.5$.

(b) Isotropic velocity ($\lambda=1$) and anisotropic damping ($\mu=\mu_0/\cos^2\theta$): $D=0.167$.

(c) Anisotropic velocity ($\lambda=8$) and isotropic damping ($\mu=\mu_0$): $D=0.63$.

(d) Anisotropic velocity ($\lambda=8$) and anisotropic damping ($\mu=\mu_0/\cos^2\theta$): $D=0.0018$.

The value of $F(\Theta/T)$ at $T=1.5$ K is 0.99. The theoretical correlation times from Eq. (31) are then as follows:

$$\tau_c=5.6\times10^{-10} , \quad (34a)$$

$$\tau_c=1.7\times10^{-9} , \quad (34b)$$

$$\tau_c=4.4\times10^{-9} , \quad (34c)$$

$$\tau_c=1.6\times10^{-7} \quad (34d)$$

in units of seconds. We take the longest of these τ_c's, case (34d), and use it to calculate the CDW linewidth from Eq. (22). For NMR, resonance at 12 MHz ($H_0\approx6$ T), for which $w=pK_0\omega_r=2\times10^4$ sec^{-1},

$$w\tau_c\sim3\times10^{-3} . \quad (35)$$

The motionally narrowed CDW linewidth is then, *at most*,

$$\Delta H_{\rm CDW}=34(w\tau_c)=0.1 \text{ Oe} . \quad (36)$$

This value is consistent with the observed linewidth 0.27 Oe at $T=1.5$ K and $H_0=6$ T.

Since the motionally narrowed CDW broadening and the dipolar broadening are expected to have Gaussian shapes, the total linewidth involves addition in quadrature:

$$\Delta H=[(0.215)^2+(34w\tau_c)^2]^{1/2} . \quad (37)$$

(0.215 Oe is the zero-field linewidth extrapolated from measurements at several H_0.[16]) The maximum contribution of the CDW to the linewidth at 1.5 K and 6 T is therefore ~0.02 Oe.

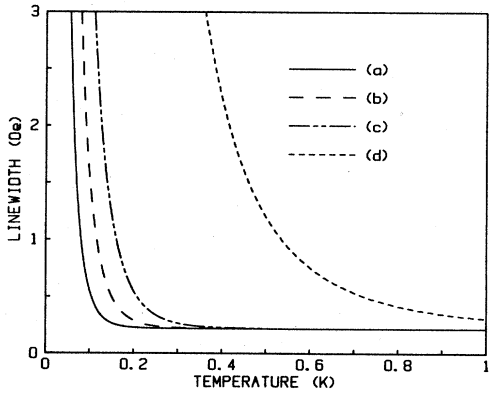

FIG. 2. NMR linewidth versus temperature for four models of phason anisotropy (described in Sec. IV). $H_0=6$ T.

V. TEMPERATURE DEPENDENCE OF ΔH

The phason excitations will, of course, subside at low temperature. Consequently, the correlation time τ_c will increase rapidly with decreasing T. The CDW broadening should then come in dramatically. The theoretical behavior, based on Eqs. (31) and (37), is shown in Fig. 2 for the four models described above. It is clear that measurements below 100 mK should be attempted to investigate whether (or not) this interesting phenomenon occurs.

There is also the possibility that at some (low) temperature the CDW may become pinned by lattice imperfections. In such a case there would be a sudden increase in NMR linewidth, and the profile of Fig. 1 might then emerge.

The spin-lattice relaxation time T_1 should also be affected by CDW phase excitations. The dominant mechanism would probably involve quadrupole coupling, since the Knight-shift fluctuations cause hyperfine fields parallel to $\mathbf{H}_0$. We have not investigated these questions in detail.

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[14]From an experimental view the most crucial problem is observation of the CDW satellites. These diffraction spots are smaller than Bragg reflections by $\sim 10^5$, and lie very close to the Bragg spots. (See Ref. 4.) Sufficiently sensitive experiments have not been reported.

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