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NMR search for charge density waves*

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We show that the presence of a static charge density wave (CDW) should have pronounced effects on the NMR spectrum of a metal, such as potassium. With a thermally fluctuating CDW, the effects are averaged out, but may leave a residual contribution to the linewidth. Observed NMR spectra in potassium metal rule out the presence of a static CDW, but do not rule out the existence of a thermally fluctuating CDW. Our linewidth data combined with spin-lattice relaxation data of others require that the axis of the charge density wave be parallel to the applied field and that thermal fluctuations be rapid enough to produce correlation times less than 1.3×10^{-7} sec at 1.5 K. We are able to account for our linewidth (0.215 ± 0.015 G) with interactions characteristic of the uniform-density conduction-electron state.

I. INTRODUCTION

The usual first approximation for the electronic state of a simple metal is a nearly-free-electron gas with uniform charge and spin density throughout the metal. However, Overhauser[1,2] has considered sinusoidal variations from the uniform model. We are here considering the case of a charge-density wave (CDW), whose theory he has developed.[3-5] Such an electronic state has been proposed for potassium to explain experimental observations which the uniform-electron-density model is thought unable to account for. The experimental results supporting and disagreeing with the CDW explanation have been discussed elsewhere,[4-7] as have other possible explanations.[6,8]

In this paper, we consider the effect of a CDW on the NMR spectrum of potassium. We first present the nature of the electronic state proposed by Overhauser. We show that a static CDW should have marked effects on the nuclear resonance due to the electric quadrupole and hyperfine couplings between the nuclei and the conduction electrons.

Thermal fluctuations of the static CDW have also been proposed[4,5,9] to explain experimental data. We find that even in the presence of fluctuations, the CDW can influence the NMR spectrum by producing broadened linewidths, provided the fluctuations are not too severe, and contributing to spin-lattice relaxation.

We present potassium nuclear resonance linewidth data, and examine it for evidence of a CDW. No clear evidence is found for a CDW in K, and we are able to account for the linewidths with conventional broadening mechanisms. We discuss spin-lattice relaxation measurements of Narath and Weaver[10] and of Kaeck.[11] The NMR data do not rule out the existence of a CDW in K, but do place restrictions upon its orientation and the thermal fluctuations which must necessarily accompany it.

Since Overhauser's first proposal of the possibility of CDW's they have been found in the transition-metal dichalcogenides. They were first seen by Gossard and Ehrenfreund[12] in $\mathrm{NbSe_2}$ as quadrupole splittings of the Nb^{93} NMR, and subsequently have been seen in electron diffraction by Wilson and diSalvo[13] in a variety of other such layer materials. The general considerations in our paper concerning the possible ways CDW's might manifest themselves in NMR should apply to those compounds as well. This fact has given us added incentive to publish our negative results.

II. ELECTRONIC STATE OF CDW

Overhauser has considered an electron gas with a sinusoidal oscillation in the electron density; for point $\vec{r}$ in the metal,[3]

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

where ρ_0 is the average electron density, p is the amplitude of the oscillation relative to ρ_0, and $\vec{Q}$ is the wave vector of the oscillation. He has shown that this oscillation of $\rho(\vec{r})$ requires an oscillatory potential in the one electron Hamiltonian of the form

$$V(\vec{r}) = -G\cos(\vec{Q}\cdot\vec{r}), \tag{2}$$

and has used this potential to do a self-consistent Hartree-Fock calculation.

The quantities p, G, and Q are treated as parameters. Their values are chosen by requiring self-consistency of the calculation and by minimizing the total electron energy. This results in relations between the parameters. The CDW wave vector is slightly larger than the diameter of the Fermi surface, and is given by

$$Q \approx 2k_f(1 + G/4E_F), \tag{3}$$

where k_F and E_F are the Fermi wave vector and

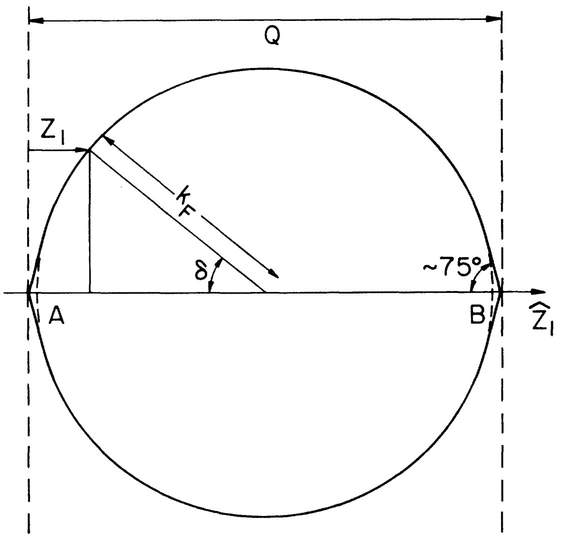

FIG. 1. Proposed Fermi surface for potassium with a charge-density wave. There is slight conical distortion at points A and B ($k_{z_1} = \pm\frac{1}{2}Q$). The average over the Fermi surface of $|\psi(\vec{R})|^2$ is approximated by averaging over the shape of radius k_F.

energy. The oscillation amplitude p is related to G by

$$p = \frac{3G}{4E_F}\left[1 + \left(\frac{1-u^2}{2u}\right)\ln\left(\frac{u+1}{u-1}\right)\right], \tag{4}$$

where

$$u \equiv Q/2k_F \approx 1 + G/4E_F. \tag{5}$$

The effect of the oscillatory potential is to give a mixing of plane-wave states with wave vectors $\vec{k}$ and $\vec{k} \pm \vec{Q}$. For $\vec{k} = \pm\frac{1}{2}\vec{Q}$, the potential produces a band gap of width G. Let $\vec{Q}$ be in the $\vec{z}_1$ direction. The gaps occur at two planes in $\vec{k}$ space given by $k_{z_1} = \pm\frac{1}{2}\vec{Q}$ (see Fig. 1). Minimization of the total electron energy results in a slightly nonspherical Fermi surface with conical distortions along the $\vec{z}_1$ axis just touching the two energy gaps. Using optical data to obtain an energy-gap value of 0.62 eV for potassium, Overhauser[14] obtains $p = 0.17$ for the fractional amplitude of the electron density oscillations.

III. EFFECTS OF STATIC CDW ON NMR SPECTRUM

A. Knight-shift variations

The Knight shift (K) due to the conduction-electron spin susceptibility has been shown to be given by[15]

$$K = \tfrac{8}{3}\pi\langle\, |\psi(\vec{R})|^2\rangle_{E_F}\chi_e^S, \tag{6}$$

where χ_e^S is the conduction-electron spin susceptibility and $\langle\ \rangle_{E_F}$ denotes an average over the Fermi surface of $|\psi(\vec{R})|^2$, the conduction-electron density at nuclear site $\vec{R}$. Unlike the normal paramagnetic conduction-electron state, a CDW would be expected to give a different shift at different nuclear sites.

The wave functions for the CDW state are given by[2]

$$\phi_k = \cos\theta\, e^{i\vec{k}\cdot\vec{r}} + \sin\theta\, e^{i(\vec{k}+\vec{Q})\cdot\vec{r}}, \tag{7}$$

where

$$\sin\theta\cos\theta \equiv G/4(\mu^2 z_1^2 + \tfrac{1}{4}G^2)^{1/2},$$

$$\mu \equiv \hbar^2 Q/2m,$$

and z_1 is defined in Fig. 1. To account for the Bloch character of the wave function near a nucleus, we multiply ϕ_k by a Bloch function u_k:

$$\psi_k(\vec{r}) = u_k(\vec{r})\phi_k(\vec{r}). \tag{8}$$

We shall be evaluating ψ_k and u_k at nuclear sites $\vec{r} = \vec{R}$; we make the assumption that we can neglect any $\vec{k}$ dependence of u_k on the Fermi surface, and that it is the same for all nuclear sites. We denote its squared absolute value by $|u(O)|^2$. The quantity we are interested in is

$$|\psi_k(\vec{R})|^2 = |u(O)|^2 \times[1 + 2\sin\theta\cos\theta\cos(\vec{Q}\cdot\vec{R})]. \tag{9}$$

The first term gives the average Knight shift as for normal metals; the $\cos(\vec{Q}\cdot\vec{R})$ term is a modulation of this shift which depends upon whether the particular nuclear site is in a valley $[\cos(\vec{Q}\cdot\vec{R}) = -1]$ or a peak $[\cos(\vec{Q}\cdot\vec{R}) = +1]$ of the electron density wave.

Instead of averaging over the conically distorted Fermi surface, we use a sphere of radius k_F as shown in Fig. 1. The modulation from the conical caps can be shown to contribute a very small fraction of the charge-density oscillations; averaging $|\psi(\vec{r})|^2$ over the sphere's volume can be shown to give the ~17% modulation stated by Overhauser.[3-5] To average, we integrate the quantity times the increment of surface area $d^2k = 2\pi k_F^2 \sin\delta\, d\delta$. Then using $z_1 = k_F(1-\cos\delta)$, the integral needed is

$$2\frac{G}{4}\int_0^{\pi/2} \frac{2\pi k_F^2 \sin\delta\, d\delta}{[\mu^2 k_F^2(1-\cos^2\delta)^2 + \frac{1}{4}G^2]^{1/2}},$$

for integration over the left half of the Fermi surface (the right half gives the same result). To obtain the average, we divide by the area of the left hemisphere, $2\pi k_F^2$. The resulting average is

$$\langle 2\cos\theta\sin\theta\rangle_{E_F} = \frac{G}{2\mu k_F}\ln\left(\frac{1 + (1 + G^2/4\mu^2 k_F^2)^{1/2}}{G/2\mu k_F}\right). \tag{10}$$

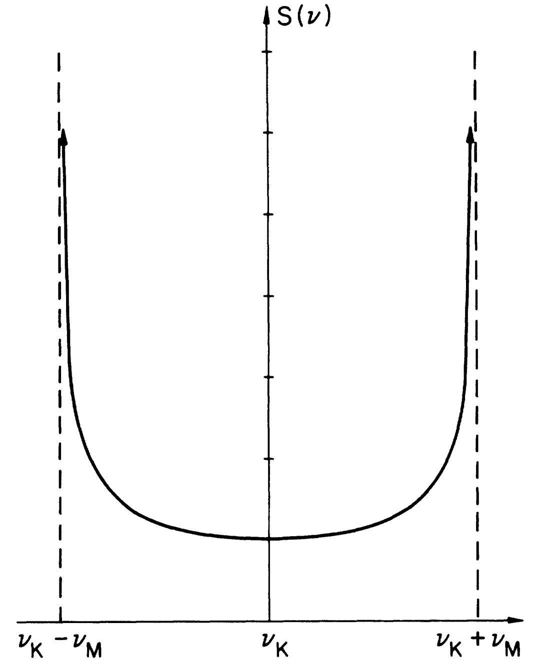

FIG. 2. Nuclear intensity distribution for a Knight shift $K(\vec{R}) = K_0 + K_M \cos(\vec{Q}\cdot\vec{R})$. The shape of the function is correct for any nuclear shift $\alpha \cos(\vec{Q}\cdot\vec{R})$.

For potassium, Overhauser[3-5] uses $G = 0.62$ eV and $E_F = 2.1$ eV. Then from (3), $Q \approx 2k_F(1+0.074)$, and $G/2\mu k_F = 0.068$, giving $\langle 2\cos\theta\sin\theta\rangle_{E_F} \approx 0.23$. The Knight shift at nuclear site $\vec{R}$ is then expected to be

$$K(\vec{R}) = \tfrac{8}{3}\pi\chi_e^S|u(O)|^2[1+0.23\cos(\vec{Q}\cdot\vec{R})]. \tag{11}$$

It is predicted to vary with crystal position of the nucleus, having a sinusoidal modulation about an average value,

$$K_0 = \tfrac{8}{3}\pi\chi_e^S|u(O)|^2. \tag{12}$$

In this treatment, we have assumed that the spin susceptibility is the same for all electrons at the Fermi surface regardless of their position on the surface. This is acceptable since the electron scattering time is expected to be less than the spin-lattice relaxation time of the electron spin susceptibility ($\tau_{\text{el}} < T_1|_{\text{el}}$).

The sinusoidal distribution of Knight shifts gives a distinguishing lineshape. We obtain it from

$$\frac{dN}{d\nu} = \frac{dN}{dR}\frac{dR}{d\nu}. \tag{13}$$

The first term is the number of nuclei per unit length in the crystal. The second can be evaluated using

$$\nu \propto \cos(\vec{Q}\cdot\vec{R}).$$

One then obtains a normalized frequency distribution in an applied field H_0

$$S(\nu-\nu_K) = \pi^{-1}\{1-[(\nu-\nu_K)/\nu_M]^2\}^{-1/2}, \tag{14}$$

where

$$2\pi\nu_K \equiv \gamma(1+K_0)H_0$$

is the center of the distribution and

$$2\pi\nu_M = 0.23\ \gamma K_0 H_0$$

is the amplitude of the sinusoidal variation. This distribution is shown in Fig. 2.

To measure the width of this distribution, we use the observed[16] Knight shift, $K_0 = 0.26\%$. In an applied field $H_0 = 60$ kG, the average Knight shift is $K_0H_0 = 156$ G, and the modulation amplitude is $0.23\ K_0H_0 \approx 36$ G, giving a distribution of Knight shifts with a full width of ~ 72 G.

B. Electric quadrupole perturbations

A second perturbation of the NMR spectrum comes from the electric quadrupole interaction with the electric field gradients set up by the CDW's oscillatory charge distribution. We treat the electric field gradients as being due to two sources: the oscillatory conduction electron charge distribution and the ion cores, which would relax from their cubic symmetry sites to partially cancel the electric fields of the first source.

1. Calculation of electric field gradients

a. Conduction electrons. The oscillatory charge density of the CDW is given by

$$\Delta\rho = p\rho_0\cos(\vec{Q}\cdot\vec{r}). \tag{15}$$

A one-dimensional model gives for Poisson's equation

$$eq \equiv \frac{dE}{dx} = -\frac{d^2V}{dx^2} = -4\pi p\rho_0\cos(\vec{Q}\cdot\vec{r}), \tag{16}$$

where V and E are the electrostatic potential and electric field due to the oscillatory charge density. The distribution of electric field gradients has a sinusoidal variation with a maximum value $q_{\max} = 4\pi p\rho_0/e$. Using lattice parameter data[17] to compute ρ_0 gives $q_{\max} = 3.00\times10^{22}$ cm^{-3}.

b. Ion cores. The ion cores are expected to be shifted from their cubic symmetry positions to partially cancel the electric fields of the conduction electrons. The displacements which would cancel the electric fields are given by[5]

$$\vec{u}(\vec{L}) = (p\vec{Q}/Q^2)\sin(\vec{Q}\cdot\vec{L}), \tag{17}$$

for an ion associated with cubic site $\vec{L}$. The maximum value for this displacement is

$$|\vec{u}|_{\max} = P/Q = 1.055\times10^{-9}\ \text{cm}. \tag{18}$$

To estimate the ions' electric field gradients, we use the gradient in the radial direction from an ion of charge e:

$$\frac{dE}{dr} = \frac{2e}{r^3}. \tag{19}$$

The maximum gradient will come when the ion is displaced along this radial direction from the point in question: $r = L \pm u$.

To obtain an upper limit on the gradient, we use this approximation for each lattice site. Then (for $u/L \ll 1$)

$$\frac{dE}{dr} \approx \frac{2e}{L^3}\left(1 \pm 3\frac{u}{L}\right). \tag{20}$$

The first term is the gradient of the ions in their undisplaced sites. The cubic symmetry of the undisplaced lattice gives zero for this term when summed over all lattice sites. It is the displacement term which produces the nonzero electric field gradient of the ions. In summing this term over lattice sites, we neglect the tensor nature of the true problem to obtain an upper limit. Then

$$q_{\text{ions}} < 6 \sum_L \frac{u}{L^4}. \tag{21}$$

To estimate the lattice sum, we use the contributions from the first neighbors ($n = 8$, $L = 4.525\times10^{-8}$cm) and second neighbor[17] ($n = 6$, $L = 5.225\times10^{-8}$cm). This gives $q_{\text{ions}} \lesssim 1.72\times10^{22}\ \text{cm}^{-3}$. This value is comparable to the electron contribution, but is overestimated.

The total q would be a tensor sum of the two contributions, and would have a magnitude which is less than the arithmetic sum. Since the expected ion contribution to q is less than that of the conduction electrons, we take the contribution of the electrons as an estimate of the total electric field gradient.

We need finally to take account of the Bloch nature of the conduction electron states, and of the fact that the nuclei which sample the gradients are at the center of potassium ion cases. The presence of electric field gradients distorts the core and causes the gradient at the nucleus to be amplified by $(1+\gamma^S)$, where γ^S is the Sternheiner antishielding factor, estimated[18] to be $(1+\gamma^s) \sim 18.2$ for gradients due to charges outside the ^{39}K ionic radius. In treating electric field gradients in copper metal, Kohn and Vosko[19] find important contributions from excess charges inside the ionic radius, where $\gamma^S = O$. However, the Bloch nature of the true conduction electron states amplifies the gradient experienced by the nucleus. Their work corrects the field gradients computed from plane wave states by multiplying by an amplification factor α which they estimate to be ~ 25.6 for copper. Since such core amplification factors are expected to increase with increasing nuclear charge (as do Knight shifts in metals, for instance), we scale their factor with $Z(=19$ for potassium, 29 for copper) to obtain $\alpha \sim 17$ for potassium. This then gives

$$q_{\max}^{\text{nuclear}} \approx 5.1\times10^{23}\text{cm}^{-3}.$$

2. First-order quadrupole shifts

When treated as a first-order perturbation on the nuclear transitions of the $I = \frac{3}{2}$ potassium nucleus with quadrupole moment Q', the central transition $(\frac{1}{2} \leftrightarrow -\frac{1}{2})$ is unaffected, but the outer two transitions $(\pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2})$ are. The first-order shifts[15] go as $\frac{1}{2}(3\cos^2\theta - 1)$, where θ is the angle between the applied field $\vec{H}_0$ and the field gradient direction. Considering $\theta = 0$, the transitions are shifted by $\pm\nu_Q$ where

$$\nu_Q \equiv 3e^2qQ'/2I(2I-1)h. \tag{22}$$

Using $Q' = 0.07\times10^{-24}e\ \text{cm}^3$ gives $\nu_Q^{\max} = 6.26\times10^5$Hz, or using 1.987 MHz (10kG) for ^{39}K gives a splitting of ~ 3100 G. Since $q(\vec{R}) = q_{\max}\cos(\vec{Q}\cdot\vec{R})$, the distribution of field gradient shifts of the outer ^{39}K transitions would have the shape functions of Fig. 2, but with infinities at $\sim \pm 3100$ G (for $\theta = 0$).

There is evidence which indicates that if a CDW is present in potassium, its wave vector $\vec{Q}$ (and hence the direction of q) attempts to align along $\vec{H}_0$. If it does not align, a continuous distribution of angular orientations would be present in a powdered sample. A first-order quadrupole powder pattern would then have to be weighted with the above distribution of electric field gradients to obtain the NMR line shape. In either case, we have demonstrated that a CDW should have a marked effect on the outer ^{39}K transitions; they should be "wiped out" of the central transition.

3. Second-order quadrupole shift

The strength of the field gradients calculated in Sec. III B 1 requires considering second-order perturbation theory. If we assume that $\vec{Q} \| \vec{H}_0$ and that the electric-field-gradient tensor has axial symmetry ($\eta = 0$) at all nuclear sites, then the central transition $(+\frac{1}{2} \leftrightarrow -\frac{1}{2})$ remains unaffected by the electric field gradient.[15] To have $\eta = 0$ would presumably require $\vec{H}_0$ (and $\vec{Q}$) to be in the [100] directions for the bcc potassium lattice.

If the principal gradient direction does not lie along $\vec{H}_0$ but is random, the central transition will be spread into a powder pattern.[18] Again, we would weight such powder patterns by the distribution of electric field gradients. To obtain a measure of the width of the resulting line shape, we use $q_{\max}^{\text{nuclear}}$ (most nuclei in the sample have $q \sim q_{\max}^{\text{nuclear}}$) and a powder pattern with $\eta = 0$ for simplicity (the width of the pattern is roughly the same for all η). At a frequency of $\nu_0 = 12$ MHz (~60 kG), this pattern has a width of ~90 G for the nuclear resonance intensity.

IV. THERMALLY FLUCTUATING CDW

The previous treatment assumes a static CDW; the interaction parameters experienced by a nucleus are assumed not to change during a time of the order of several times the inverse of the splitting frequencies predicted. However, in explaining experimental results on potassium, Overhauser has assumed thermal fluctuations[4,5,9] (called phasons) of the CDW. The perturbations of a given nucleus then fluctuate between those of a maximum in the electron density and those of a minimum.

The effects of time modulating a CDW will appear in both the linewidth and the spin-lattice relaxation time T_1. We use the results of Narath and Weaver[10] and of Kaeck[11] on T_1.

It has been shown that the residual linewidth of an interaction of width $\Delta\omega_{\text{int}}$ ($\equiv \omega_{\text{int}} - \bar{\omega}_{\text{int}}$) when randomly fluctuating between $+\Delta\omega_{\text{int}}$ and $-\Delta\omega_{\text{int}}$ about its average value $\bar{\omega}_{\text{int}}$ is given by[20]

$$\Delta\omega = \Delta\omega_{\text{int}}(\Delta\omega_{\text{int}}\tau_c), \tag{23a}$$

where τ_c is the average time between fluctuations. τ_c, the correlation time, is the time over which the interaction appears to be static. Equation (23a) assumes $\Delta\omega_{\text{int}}\tau_c < 1$; as this quantity approaches 1, $\Delta\omega \to \Delta\omega_{\text{int}}$.

The spin-lattice relaxation time arising from an interaction[15] should go roughly as

$$1/T_1|_{\text{int}} = (\Delta\omega_{\text{int}})^2\tau_c/(1+\omega_0^2\tau_c^2), \tag{23b}$$

where ω_0 is 2π times the Larmor frequency. Typically either $\omega_0^2\tau_c^2$ is very much larger or very much smaller than 1 giving us

$$\omega_0^2\tau_c^2 \gg 1, \quad 1/T_1|_{\text{int}} = \Delta\omega_{\text{int}}^2/\omega_0^2\tau_c \tag{23c}$$

$$\omega_0^2\tau_c^2 \ll 1, \quad 1/T_1|_{\text{int}} = \Delta\omega_{\text{int}}^2\tau_c\,. \tag{23d}$$

In the latter case $T_1 = T_2$.

In treating a thermally fluctuating CDW, we shall have to consider several possibilities. The first question involves the alignment of $\vec{Q}$: we treat the case of $\vec{Q} \parallel \vec{H}_0$ (Sec. IV A) and the case of random orientation of $\vec{Q}$ (Sec. IV B). Within either case, we must consider three perturbations: (i) the Knight shift, (ii) first-order quadrupole, and (iii) second-order quadrupole. Finally, we must consider whether the resonances observed contain all three transitions of the $I = \frac{3}{2}$ nucleus, or whether the outer transitions ($\pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2}$) are "wiped out" of the observed resonance, either by the CDW's quadrupole interactions, or by strains and lattice imperfections as in copper.

A. $\vec{Q} \parallel \vec{H}_0$

1. Knight shift

The theory of the oscillatory Knight shift does not involve the direction of $\vec{Q}$, and yields the same result for both Secs. IV A and IV B. Furthermore, it is correct whether or not the outer transitions are within the observed linewidth. The Knight shift will shift the average resonance position to a frequency

$$\bar{\omega}_{\text{int}} = 2\pi\nu_K = \gamma(1+K_0)H_0 \tag{24}$$

and will have an interaction width given by

$$\Delta\omega_{\text{int}} = \gamma(0.23K_0)H_0. \tag{25}$$

This will produce a contribution to the motionally narrowed linewidth which is proportional to H_0^2.

An isotropic Knight shift is equivalent to adding a field parallel to the applied field. Hence a fluctuating isotropic Knight shift does not induce spin flips and thus does not cause spin-lattice relaxation.

If there is an anisotropic component, it can produce spin-lattice relaxation providing it is not axially symmetric about the $\vec{H}_0$ direction. For $\vec{Q} \parallel \vec{H}_0$, however, we expect that axially symmetric case.

2. Quadrupole interactions

For $\vec{Q} \parallel \vec{H}_0$, our model assumes that the direction of the largest component of the electric-field-gradient tensor is parallel to $\vec{H}_0$. For an assumed axially symmetric tensor, the quadrupole Hamiltonian is then diagonal in the m_I levels of the nucleus. The frequency of the central transition ($+\frac{1}{2} \leftrightarrow -\frac{1}{2}$) is unaffected by the quadrupole interaction and given by Eq. (24). The outer transitions ($\pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2}$) are shifted by $\pm\nu_Q$, respectively. There is no effect on the spin-lattice relaxation time since the quadrupole matrix elements are diagonal.

Considering all three transitions, the average frequency shift due to the quadrupole interaction is zero. The outer transitions will have an average interaction width given approximately by

$$\Delta\omega_{\text{int}} \approx 2\pi\nu_Q^{\max}. \tag{26}$$

The quadrupole interaction for this alignment of $\vec{Q}$ will produce a contribution to the narrowed linewidth which is independent of applied field.

The above treatment assumes that the outer transitions occur within the observed nuclear resonance linewidth. If they are "wiped out" by strains and lattice imperfections, or by a CDW which is not rapidly fluctuating, the quadrupole interaction will contribute to neither an average frequency shift nor to a residual linewidth.

B. Random orientation of $\vec{Q}$

1. Knight shift

The theory of the Knight shift remains as discussed in Sec. IV A. Again, we stress that it holds independent of whether or not the outer transitions fall within the experimentally observed linewidth. For the isotropic component there can be no T_1 contribution. An anisotropic term will be expected to contribute. Probably a reasonable upper limit for the anisotropic term is 30% of the isotropic.

2. First-order quadrupole perturbation

For a random orientation of $\vec{Q}$, most of the powder sample crystallites are perpendicular to the applied field (the distribution of orientations goes as $\sin\theta\, d\theta$, which peaks at 90°). At this orientation, an electric field gradient with strength ν_Q produces a shift of approximately

$$\Delta\omega_{\rm int} \cong \tfrac{1}{2}(2\pi\nu_Q^{\max}). \tag{27}$$

As before, due to the opposite shift directions of the $(+\frac{3}{2}\leftrightarrow+\frac{1}{2})$ and $(-\frac{3}{2}\leftrightarrow-\frac{1}{2})$ transitions, first-order perturbation theory produces no net shift of the resonance position.

Again, (23b) describes the spin-lattice interaction with $\Delta\omega_{\rm int}$ given by (27).

3. Second-order quadrupole perturbation

As discussed in Sec. III B 3, the nuclei perturbed by $q^{\max}$ produces a powder pattern ~90 G wide at $\nu_0 = 12$ MHz. We would thus expect

$$\Delta\omega_{\rm int}\ (\text{at } 12\text{ MHz}) \approx \gamma \times (45\text{ G})\ . \tag{28}$$

Since this perturbation goes as H_0^{-1}, it would produce a linewidth contribution proportional to H_0^{-2}.

In second-order perturbation theory, the quadrupole interaction yields a net average shift of the resonance position. For a nucleus where principle quadrupole axis makes an angle θ with respect to $\vec{H}_0$, Cohen and Reif[18] give the second-order shift of the central transition for $I=\frac{3}{2}$ as

$$\nu^{\rm int} = (-3\nu_Q^2/16\nu_0)(1-\cos^2\theta)(9\cos^2\theta-1)\ . \tag{29}$$

When averaged over a $\sin\theta\, d\theta$ distribution of orientations, we obtain

$$\bar{\nu}^{\rm int} = -\nu_Q^2/10\nu_0 \approx -(\nu_Q^{\max})^2/10\nu_0\ . \tag{30}$$

We might then expect to see a shift of the resonant position which is proportional to H_0^{-1}, even in the presence of thermal fluctuations. We have considered the effect of a thermally fluctuating quadrupole interaction upon the frequency of the central transition using density-matrix formalism. The results depend upon the product $\omega_0^2\tau_c^2$.

a. $\omega_0^2\tau_c^2 \gg 1$. In this limit, the quadrupole interactions appear static and produce the expected shift proportional to H_0^{-1}.

b. $\omega_0^2\tau_c^2 \ll 1$. In this rapid fluctuation limit, the quadrupole interaction produces a shift proportional to H_0, but also produces nuclear relaxation, giving line broadening. The broadening is much larger than the shift, which would then go undetected.

Hence unless the CDW is static, i.e., τ_c is long with respect to a Larmor period, we do not expect to see frequency shifts as predicted by Eq. (30).

V. EXPERIMENTAL METHOD

A. Samples

Samples were prepared by forming a dispersion of small "beads" of potassium in mineral oil. This technique has been used in previous NMR studies of alkali metals. The potassium metal was purchased from Mine Safety Appliances (5-g ingot, 99.95% purity). It was heated and melted in 200 cm^3 of degassed, lightweight mineral oil (a lightweight oil is needed so that the metal particles can be separated from the oil by centrifuging). With 0.5 cm^3 of oleic acid added to act as a dispersing agent and to prevent coagulation, the components were stirred with an apparatus made and described by Asik.[21] The resulting dispersion was viewed under a microscope and was found to consist of small "silver-colored" spheres of potassium metal, approximately 10 μ in diameter.

The dispersion was centrifuged and the potassium residue put into cylindrical nylon coil forms. To diminish the line broadening due to magnet inhomogeneity, small sample sizes ($\frac{1}{8}$ in. diam, $\frac{1}{8}$ in. length, and $\frac{1}{4}$ in. diam, $\frac{1}{4}$ in. length) were used.

B. Spectrometer

A hybrid junction spectrometer[22] was used to measure the potassium linewidth. For the frequencies studied (4.45–12 MHz), a capacitor-divider tuning arrangement was used. The electronics of this spectrometer are described elsewhere.[23] To connect the capacitor-divider to the sample coil, a ~1-m length of Microdot cable (No. 275-3932) was used. The magnet was a Westinghouse superconducting solenoid with a liquid-helium sample chamber. This allowed measurements at 4.2 and 1.5 K (obtained by pumping on the helium).

C. NMR measurements

Since only a single narrow resonance is observed instead of the structure predicted in Sec. III B 2, we can only hope to obtain information on a possible CDW state through its motionally narrowed residual linewidth. Since the residual linewidth due to the Knight-shift variation would be expected to go as H_0^2 and the residual second-order quadrupole broadening as H_0^{-2}, we have studied the linewidth as a function of H_0.

We utilize the spin-lattice relaxation data of Kaeck[11] and of Narath and Weaver.[10] Kaeck found $T_1T = 23.3$ sec K, whereas Narath and Weaver got $T_1T = 27 \pm 1$ sec K. Both worked in the temperature range 1.1–4.2 K. There does not appear to be any particular difference in the experiments except that Narath and Weaver worked at higher frequencies where they should have had a somewhat better signal to noise. For simplicity, we use the Narath and Weaver number. In their analysis, these authors point out that their result agrees reasonably well with values predicted from the Korringa relation, indicating there is no reason tc believe the T_1's arise from any cause other than the usual conduction electron spin-flip mechanism.

In a continuous wave measurement of the linewidth, we must take care that the measurement itself does not broaden the resonance. The first source of such broadening is field inhomogeneity, but we must also include possible effects due to modulation (amplitude and frequency), phase of the signal [we want complete absorption (χ'')], saturation, and lock-in time-constant effects.

The measurements were begun at 8 MHz (~40 kG). The field was varied until the resonance was found. Then the superconducting solenoid was put into the persistent mode. The variable rf phase of the spectrometer was adjusted for an antisymmetric derivative signal ($d\chi''/dH$). The signal height was studied versus rf level to observe saturation. The rf level was then set ~ − 10 db below saturation (a factor of 3 in H_1). The modulation amplitude was varied in factors of 2 and the linewidth measured each time. When no difference in linewidth was noted between two such measurements, the lower amplitude was used. To avoid modulation sidebands,[24] the modulation frequency for all final measurements was 4 Hz (equivalent to 0.02 G for potassium). The sweep rate was similarly varied by factors of 2 to insure that the lock-in time constant was not broadening the resonance. Time constants of 1 and 3 sec were used with final sweep rates slow enough that there were greater than ten time constants between the derivative extrema.

Five parameters could be varied to minimize field inhomogeneity: axial position of the sample coil for correcting gradients in this direction, shim coil corrections for gradients in directions perpendicular to the solenoid axis (dH_0/dx, dH_0/dy), and a shim coil for second-order corrections in the z direction (d^2H_0/dz^2). The linewidth was first studied as a function of sample position, and a minimum obtained. Then the previously set parameters were checked to see that they were not contributing to the new width. The position was then rechecked to see if the minimum position had changed.

The shim coil currents were then varied (with both current polarities) until the minimum linewidth was obtained. Again, the previously set parameters were checked after each shim coil was optimized to obtain the narrowest possible line, and the optimum shim current rechecked afterward. When all settings had been optmized, it was found that no current was needed in the dH_0/dz shim coil, which confirmed our positioning of the sample.

To obtain numerical results for the linewidth, the sweep width was calibrated by changing the spectrometer frequency. The resonance was observed on the same sweep at three frequencies to check sweep linearity.

The linewidth was measured between 22.25 and 60 kG. The optimum shim coil currents were found to scale with field as expected.

VI. RESULTS

The result of these measurements at 4.2 K is shown in Fig. 3. Most were taken with the $\frac{1}{8}$-in. sample, but at 22.25 and 60 kG, data were taken with the $\frac{1}{4}$-in. sample. Note that the larger sample locates $\sim 2^3 = 8$ times as much sample in the more inhomogeneous regions or field (away from the sample center) than the $\frac{1}{8}$-in. sample. If we assume a field-independent linewidth, we extrapolate to zero field, giving additional preference to the low-field data and the larger sample. We then obtain $\Delta H|_0 = 0.215 \pm 0.015$ G peak to peak. With the same shim settings as for the $\frac{1}{8}$-in. sample, the measured linewidth for the $\frac{1}{4}$-in. sample at 60 kG is 0.292 ± 0.012 G. This is $\sim\sqrt{2}$ times the zero-field value. If we add the true sample linewidth and the inhomogeneity linewidth contribution as the sum of squares to obtain the squared observed linewidth, we obtain an inhomogeneous width of ~0.2 G at 60 kG for the $\frac{1}{4}$-in. sample and ~0.009 G at 22.25 kG for the $\frac{1}{8}$-in. sample, thus adding confidence to our zero-field value.

We have also measured the linewidth at 1.5 K for the $\frac{1}{8}$-in. samples. The results were the same as 4.2 K.

VII. CDW ANALYSIS

We are unable to clearly distinguish a component to the linewidth which is proportional to H_0^2 or H_0^{-2}. The high-field linewidths of Fig. 3 are broader, but the increase is of the order of the error bars and of the scatter in the points. A linear dependence, possibly due to a slight bit remaining field inhomogeneity is not ruled out. We, therefore, assume that any field-dependent CDW broadening of the resonance is less than the observed linewidth and is undetected. We can then analyze the observed width for the cases discussed in Sec. IV.

A. $\vec{Q} \parallel \vec{H}_0$

1. Knight shift

The Knight-shift variation at 60 kG gives $\Delta\omega_{\text{int}} \approx (36\text{ G})\times\gamma = 4.5\times10^4\text{ sec}^{-1}$. Then setting $\Delta\omega_{\text{int}}^2\tau_c < \gamma\Delta H|_{60\text{ kG}}$ gives $\tau_c < 1.3\times10^{-7}$ sec from linewidth.

Utilizing $\tau_c \leq 1.3\times10^{-7}$ gives $(\omega_0\tau_c)^2 < 100$. Thus either (23c) or (23d) apply. If we assume there to be an anisotropic Knight shift which is 30% of the isotropic one $\Delta\omega_{\text{int}} = 0.30\times4.5\times10^4\text{ sec}^{-1} = 1.4\times10^4\text{ sec}^{-1}$. If $(\omega_0\tau_c)^2 \gg 1$, Eq. (23c) gives $T_1 = 3.7$ sec. This result is too short compared to the measured time, but *if* $\Delta\omega_{\text{int}}$ is even smaller, the T_1 would be longer so that $\tau_c < 1.3\times10^{-7}$ is possible.

If we assume $\omega_0^2\tau_c^2 \ll 1$, the fluctuating anisotropic part would make $\tau_c \leq 2\times10^{-10}$ sec. But a weaker anisotropic value permits τ_c to be longer, (up to $\tau_c \sim 1/\omega_0 = 1.3\times10^{-8}$ sec).

All told, then, we conclude $\tau_c < 1.3\times10^{-7}$.

2. First-order quadrupole perturbation

If we assume that the outer transitions are present in our signal (they account for 0.6 of the total nuclear resonance intensity), then the predicted 3100-G first-order quadrupole spread is used for $\Delta\omega_{\text{int}}$. We then obtain $\tau_c < 1.8\times10^{-11}$ sec.

B. Random $\vec{Q}$

1. Knight shift

The Knight-shift analysis of Sec. VII A applies to random $\vec{Q}$ as well. We stress that its results hold independently of quadrupole broadening by either CDW or sample stains. It gives $\tau_c \leq 1.3\times10^{-7}$ sec.

2. First-order quadrupole perturbation

Most randomly oriented $\vec{Q}$'s fall at right angles to $\vec{H}_0$ and reduce $\Delta\omega_{\text{int}}$ by a factor of 2 from the value in Sec. VII A 2. This gives values for τ_c of $\tau_c < 7.2\times10^{-10}$ sec from linewidth if we assume we are observing all transitions.

Using this τ_c we get $(\omega_0\tau_c)^2 \ll 1$. Thus the spin-lattice relaxation time obeys (23d). For $\omega_{\text{int}} = 3.6\times10^6$ and $T_1 > 24$ sec we find $\tau_c < 3.2\times10^{-15}$ sec. We find it hard to believe τ_c could be that short for such a process, and thus conclude that if there is a charge density wave with $\vec{Q}$ not parellel to $\vec{H}_0$ we are not observing all the transitions.

3. Second-order quadrupole perturbation

The linewidth was observed at frequencies as low as 4.45 MHz. If we scale the results of Sec. IV B 3 to this frequency and set $\Delta\omega_{\text{int}}^2\tau_c$ less than the observed linewidth, we obtain $\tau_c < 1.2\times10^{-8}$ sec. Such a value makes $(\omega_0\tau_c)^2 \ll 1$, and puts us in the case of (23d). We can then look at the effect

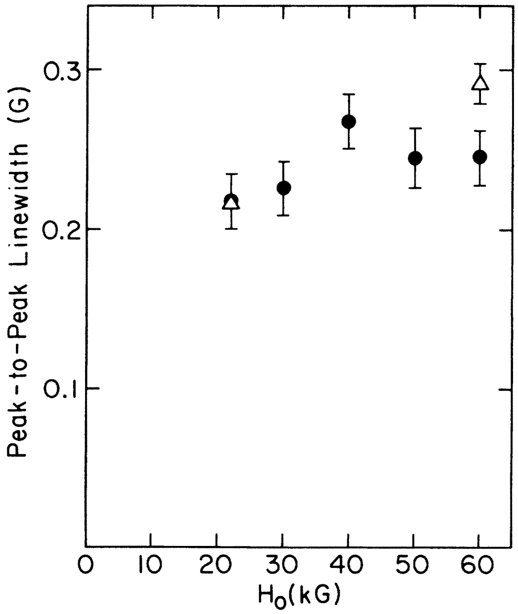

FIG. 3. Peak-to-peak linewidth of ^{39}K (potassium metal) resonance as a function of applied field H_0.

on T_1, concluding as above that $\tau_c < 3.2 \times 10^{-15}$ sec, an unreasonably short time.

We can therefore conclude that if a CDW exists in K, its axis is parallel to $\vec{H}_0$ and it has a $\tau_c < 1.3 \times 10^{-7}$ sec as deduced from Knight-shift considerations.

VIII. CONVENTIONAL LINEWIDTH ANALYSIS

A. Dipole-dipole interaction

We can attempt to account for the observed linewidth in terms of the nuclear dipole-dipole interactions. The expression for the second moment for this interaction is[25]

$$M_2 = \tfrac{3}{5}\gamma^4\hbar^2 I(I+1)\sum_k r_{jk}^{-6} \ , \tag{31}$$

where r_{jk} connects the jth nucleus with the surrounding nuclei of the crystals. Gutowsky and McGarvey[26] have done the lattice sum for body-centered cubic cells and obtain

$$\sum_k r_{jk}^{-6} = 29.03/a^6 \ , \tag{32}$$

where a is the cubic cell length. Putting in the numerical values for potassium gives

$$M_2 = 7.70 \times 10^3 \ \text{sec}^{-2} \ .$$

Two types of line shapes are often discussed in NMR: Gaussian and Lorentzian. To see which more nearly applies to potassium, we examine the ratio of the following two widths of the absorption derivative signal: (peak-to-peak separation)/(full width at half-maximum). The ratios are 0.79 and 0.40, respectively, for the Gaussian and Lorentzian shapes. Examining this ratio for the potassium resonances at the various values for H_0 gives a value of 0.5. Thus the potassium line shape appears more nearly Lorentzian than Gaussian.

For a Gaussian line shape, the second moment is finite and is related to the peak-to-peak linewidth by

$$\begin{aligned} \Delta H_{pp}\big|_{\text{Gaussian}} &= (2/\gamma)\sqrt{M_2} \\ &= 0.14 \ \text{G} \end{aligned} \tag{33}$$

for potassium. For a Lorentzian line shape, the second moment diverges; we would then expect the peak-to-peak linewidth for a nearly Lorentzian line shape to be less than that predicted by Eq. (33). However, our measured linewidth is greater than the above predicted width.

The potassium resonance has also been observed by Kaeck.[11] His free-induction decay study places an upper limit of $\Delta H_{pp} \leq 0.1$ G, and gives a Lorentzian line shape. This result gives better agreement with the second-moment calculation. We shall return to the discrepancy between his linewidth results and ours.

B. Electron-nucleus coupling

To explain our additional observed linewidth, we consider other couplings of the nuclei. Pseudoexchange coupling between like nuclear species does not lead to an increased second moment. Pseudodipolar coupling, however, does increase the second moment. To estimate its magnitude in potassium, we use the results of Poitrenaud[27] on Cs, which give a coupling constant of $B_{II}^{pd} \sim 35$ Hz. Since pseudodipolar coupling is a second-order effect mediated by the contact interaction between the nuclei and conduction electrons, we can scale its value according to

$$B_{II}^{pd} \propto (\gamma K_0)^2 \ . \tag{34}$$

The scaled result for potassium is $B_{II}^{pd} \sim 0.14$ Hz, which corresponds to $\sim 10^{-4}$ G, which is a negligible linewidth contribution.

An additional source of line broadening is the lifetime of the nuclear levels. We use the T_1 of Narath and Weaver[10] at 4.2 K to calculate $(1/\gamma)(1/T_1) = 0.000\,78$ G, a negligible contribution.

C. Lattice imperfections

The weak-field dependence (if any) of the linewidth leads us to consider an additional line-broadening mechanism, field-independent, first-order quadrupole broadening due to lattice imperfections. Abragam[28] gives the effect on the linewidth due to lattice imperfections producing electric field gradients which decrease radially as r^{-3}. For a body-centered cubic lattice, a concentration c of imperfections produces a Lorentzian distribution with a width given by

$$\Gamma = \tfrac{1}{3}\pi^2 \nu_c c \ , \tag{35}$$

where

$$\nu_c = (e^2 Q'/b^3)\alpha \tag{36}$$

for the broadening of the outside transitions of an $I = \frac{3}{2}$ nucleus, b is the first-neighbor distance, Q' is the nuclear electric quadrupole moment, and α is the amplification factor. ν_c is the quadrupole frequency due to an imperfection with charge e located at a first-neighbor site. For potassium, we obtain a peak-to-peak Lorentzian width

$$2\Gamma = 1.4 \times 10^4 c \ .$$

Setting this width equal to 0.215 G gives $c \sim 15$ ppm.

This small concentration is easily realizable. A typical analysis supplied by Mine Safety Appliances for their high-purity potassium gives traces of many metallic impurities, the largest concentrations being Si(~25 ppm), Ca(~8 ppm), and Na(~15 ppm). In view of the above calculations, it seems fortuitous to obtain such a narrow linewidth with this level of impurities.

Assuming first-order quadrupole broadening in our sample, two explanations are then possible for the difference in linewidth between Kaeck's measurement[11] (< 0.1 G) and this study (0.215 ± 0.015 G): (i) Kaeck's samples were purer than ours and had less first-order quadrupole broadening. (ii) Our samples are purer than his, with his having sufficient impurity concentrations to completely wipe out the $(\pm\frac{3}{2} \longleftrightarrow \pm\frac{1}{2})$ transitions, leaving only a nonquadrupole broadened central $(+\frac{1}{2} \longleftrightarrow -\frac{1}{2})$ transition.

IX. SUMMARY AND CONCLUSIONS

A. Static CDW

We have examined the effects of a static CDW in a metallic sample upon the metal's NMR spectrum. The spectrum is greatly influenced through magnetic hyperfine and electric quadrupole interactions with the conduction electrons.

For a sample with an incommensurate CDW wavelength, there is a continuous distribution of Knight shifts and electric field gradients between the two extremes of minimum and maximum electron density. The high probability of finding nuclei at these extremal positions tends to split the resonance line shape into two peaks.

A substance with a CDW which is commensurate with its lattice periodicity would have a finite number of unique sites, each with a unique resonance frequency. The nuclei near the electron density extrema would presumably be the most influenced by the CDW.

Regardless of the field dependence of the orientation of $\vec{Q}$ and of the particular nuclear transition being observed, the oscillatory Knight shift is expected to cause differential shifts proportional to H_0 between the resonant frequencies of the different nuclear sites. First-order quadrupole interactions provide field-independent shifts for noncentral transitions (nuclei with $I \neq \frac{1}{2}$), but the shift depends upon the orientation of the electric quadrupole tensor axes and $\vec{H}_0$. Finally, if the axis of the largest electric-field-gradient component does not align with $\vec{H}_0$, the field gradient can cause a second-order shift of the $(+\frac{1}{2} \longleftrightarrow -\frac{1}{2})$ transition. This shift would vary as H_0^{-1}, and would depend upon the exact orientation of the quadrupole tensor axes with respect to $\vec{H}_0$.

B. Thermally fluctuating CDW

Even in the presence of thermal fluctuations, the CDW's broadening of the NMR line shape may not be entirely eliminated. Each of the three above mentioned perturbations would leave a residual linewidth contribution given by $\Delta\omega = \Delta\omega_{\text{int}}^2 \tau_c$, where $\Delta\omega_{\text{int}}$ is static shift and τ_c, the correlation time, is an average time between thermal fluctuations.

Depending upon the length of τ_c, this residual width may become comparable to the resonance linewidth due to other broadening mechanisms (dipole-dipole, impurity broadening, etc.) and be detectable. Since the residual width goes as $\Delta\omega_{\text{int}}^2$, each perturbation would have a distinguishing field dependence for its residual width; Knight shift: $\Delta\omega \propto H_0^2$, first-order quadrupole: $\Delta\omega = \text{const}$, and second-order quadrupole: $\Delta\omega \propto H_0^{-2}$.

A thermally fluctuating CDW will contribute to spin-lattice relaxation unless it is axially symmetric with the axis aligned along $\vec{H}_0$.

C. Results for potassium

The large discrepancy between the observed NMR spectrum of potassium and that predicted by a static CDW immediately show that if a CDW exists in potassium, it must be fluctuating. Other experimental evidence supports this requirement also.[4,5,9]

None of the distinguishing field dependences predicted for the residual linewidth can be clearly demonstrated for our linewidth measurements on potassium. We can therefore only place upper limits on τ_c.

Of the three interactions considered we place more confidence in the Knight-shift perturbation since its average value can be measured, and our calculated variations of this shift for high and low electron density regions can be normalized to the measured shift. The calculation holds for any relative orientation of $\vec{Q}$ and $\vec{H}_0$, and regardless of which nuclear transitions are being observed. Requiring its residual width to be less than our measured linewidth gives $\tau_c < 1.3 \times 10^{-7}$ sec.

Assuming $\vec{Q} \parallel \vec{H}_0$, we can set the first-order quadrupole residual width to be less than our observed linewidth (this further assumes that we are detecting these transitions in our resonance). This requires $\tau_c < 1.8 \times 10^{-11}$ sec. For this orientation, we do not expect second-order quadrupole shifts of the central transition.

For a randomly oriented $\vec{Q}$, first- and second-order quadrupole interactions on the linewidth enable us to conclude $\omega_0^2 \tau_c^2 \ll 1$, which in turn can be applied to the formulas for T_1. From T_1 we find τ_c would need to be unreasonably short. Thus we conclude that if there is a charge density wave it's

$\vec{Q}$ must be parallel to H_0.

Thermal fluctuations of the CDW have been used to predict a new type of noise in potassium wires.[5] The failure to detect such noise[6,7] casts doubt on their existence and hence on the existence of a CDW in potassium. Our measurements are consistent with the usually accepted uniform-density electron state, though they do not rule out the existence of a CDW. If it is present, our measurements require that it fluctuate fast enough to produce correlation times at least as short as $\tau_c < 1.3 \times 10^{-7}$ sec at 1.5 K.

D. Other applications

Similar predictions of a CDW have been made for cesium metal. Its presence might be detectable with NMR at low temperatures. Since its Knight shift (1.57%) is ~ 6 times that of potassium, its residual width would be expected to be ~ 36 times larger. However, the cesium metal must be of very high purity so that impurity-induced line broadening ($\propto H_0$) from the Knight-shift oscillations around the impurities does not dominate the linewidths.

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