Search for NMR line-shape broadening by charge-density waves in potassium

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Measurements of the NMR linewidth of ^{39}K metal from 59 to 420 mK at an applied field of 1.5 T are reported in a search for the broadening by charge-density waves (CDW) proposed by Wang and Overhauser. The measurement sensitivity is such that CDW broadening can be observed (using their model parameters) if the correlation time for phason motion is greater than 8×10^{-6} s. A discussion of the methods used to ensure that spurious rf heating was not a significant factor in the experiment is provided. Within the resolution of our experiment, no evidence of line-shape broadening by CDW was observed.

I. INTRODUCTION

Important questions have been raised regarding the nature of the electronic ground state in the alkali metals. Overhauser[1,2] has proposed that the effects of exchange and correlation will make the occupation of the lowest energy Bloch levels unstable with respect to the formation of a charge-density wave (CDW). The alkali metals are candidates for having CDW's since the conduction electrons behave according to the nearly free-electron model, and their ion lattices are easily deformable, allowing for cancellation of the electron charge density. Attention has been focused on potassium, for which evidence of a CDW has been presented.[3,4]

Wang and Overhauser[5,6] have calculated the effects of a CDW on the NMR linewidth of potassium. Since the conduction-electron density in the CDW is predicted[7] to have a sinusoidal variation incommensurate with the lattice, the Knight shift should differ at each nuclear site, producing a broadening of the linewidth, provided that the CDW is static. If, however, the CDW is moving rapidly, this broadening will be motionally narrowed. The mechanism for such a narrowing is thermal excitation of CDW phasons.[8]

The predictions for the motional narrowing at a given temperature depend on CDW characteristics whose values are not well known. Wang and Overhauser use experimental data, including the results of recent work in neutron diffraction,[9] to estimate these values. With these, they predict the temperature dependence of the correlation time for Knight shift fluctuations that would provide the motional narrowing. Their earlier predictions[5] suggested that the linewidth broadening could become appreciable in the range 100–400 mK. Subsequent work[6] based upon the neutron-diffraction results indicates that it may be necessary to reach 40 mK to obtain a clear-cut test of their model. They caution that much uncertainty is present in these predictions and that further neutron-diffraction experiments may alter the predictions. Given these uncertainties, searching for a NMR linewidth broadening at temperatures above 40 mK should provide results that are relevant to the formulation of CDW models.

Other workers have observed the potassium NMR signal at low temperatures. Kaeck[10] observed a Lorentzian lineshape down to 1.3 K with a linewidth, 0.1 Oe, corresponding to the magnetic field inhomogeneities in his experiment. More extensive work on potassium at low temperature, which was also motivated by a search for CDW's, was done by Follstaedt and Slichter.[11] Using a dispersion of 99.95% pure potassium spheres, they performed continuous-wave NMR to record the absorption derivative signal at 4.2 and 1.5 K in fields ranging from 2.25 to 6 T, and found a peak-to-peak linewidth of 0.215 ± 0.015 Oe at both temperatures. From this they concluded that if a CDW is present at 1.5 K, the Knight shift fluctuations producing motional narrowing of their signal must have a correlation time less than 1.3×10^{-7} s for temperatures above 1.5 K. The CDW model currently used for predictions of the NMR lineshape falls well within this restriction.

In this paper, we report ^{39}K pulsed NMR experiments over the temperature range 59–420 mK at an applied magnetic field of 1.5 T. A linewidth of 0.294 ± 0.015 Oe was observed at all temperatures. These conditions, as discussed in Sec. II, establish a lower limit of 8×10^{-6} s to the correlation time for the detection of phason motion in our experiment. Within this limit, no evidence for CDW in K was observed down to 59 mK. This result rules out those of the earlier proposed parameters[5] which included large anisotropies in phason properties, but does not exclude isotropic ones or the revised ones based upon the neutron-diffraction experiment.[6,9]

An important part of the experiments was the steps taken to avoid excess sample heating by the rf pulses. They are described in detail in Sec. II B to validate our results and to serve as a guide for further experiments.

II. EXPERIMENTAL DETAILS AND RESULTS

A. Sample and apparatus

The potassium used in our work was purchased from Mallinckrodt, Inc., and had a nominal purity of better than 98%. We believe that using very high-purity material was not necessary, as a small concentration of im-

purities is not expected to affect the electron-electron interaction to which the CDW phase transition is attributed. They could, in fact, have the beneficial effect (in terms of this experiment) of forming pinning centers that would enhance the broadening of the NMR line in a way analogous to that reported for $Rb_{0.3}MoO_3$ by Jánossy *et al.*[12]

The form of the sample was a stack of thin sheets whose thickness (500 μm) was greater than the classical skin depth at the temperature of the measurements. (The skin depth is 45 μm at 300 K; because of the resistivity ratio, it is expected to be substantially less below 1 K.) The potassium was rolled into a sheet 0.05 cm thick under petroleum oil, and cut into squares 0.5 cm on each side. These were stacked in layers alternating with Mylar sheets to provide separation, with every fourth K layer substituted by a thin Al foil whose ^{27}Al NMR signal could be used as a field marker for sensitivity optimization, and for diagnostic tests of sample heating by the rf pulses (described in detail below). This stack was then coated with paraffin to provide further protection from contamination and an NMR coil was wound directly on the assembly. This was then mounted in the mixing chamber of a dilution refrigerator, where, upon cooling, the paraffin fractures, providing direct physical contact between the potassium and the ^{3}He-^{4}He liquid. A calibrated Speer carbon resistor in the mixing chamber was used to measure the temperature.

The linewidth was measured by recording the off-resonance ^{39}K free-induction decay (FID) signal produced by pulsed NMR at a frequency of 3 MHz. To deliver the transmitter power and receive the NMR signal a laboratory built spectrometer adapted from an earlier design[13] was used. For reasons discussed below, the signal-to-noise ratio of a single FID was low, so that averaging over many repetitions was necessary. This averaging was done with a Nicolet 1170 signal averager and the result transferred to a microcomputer for digital Fourier transform processing.

B. rf heating, sensitivity, and sample diagnostics

One of the critical requirements of this experiment was that the transient heating of the sample by the rf pulse be negligible. Since the signal was observed during the first few milliseconds after the rf pulse, it was necessary to evaluate the heating during this short period, and not merely its long-time average. Here we describe the steps taken to deal with this problem.

When one rf pulse deposits an amount of energy δE in the skin depth, there will be an average temperature rise of that volume $\langle \delta T_\delta \rangle$ given by $\langle \delta T_\delta \rangle \simeq \delta E / C_\delta$, where C_δ is the heat capacity of that part of the sample included in the skin depth. As mentioned above, the skin depth for the sample was much less than its thickness, so that only a small fraction of the sample received energy from the rf pulse. However, for our experimental conditions it is fortunate that the time it takes the heat to diffuse from the skin depth to the bulk of a sheet ($\tau_{\rm th}$) is short compared to the FID lifetime, so that the relevant rise in temperature δT is the much smaller value obtained by using the total sample heat capacity C:

$$\delta T = \frac{\delta E}{C} \ . \tag{1}$$

This time constant is estimated with the relation

$$\tau_{\rm th} = R_{\rm th} C \ , \tag{2}$$

where $R_{\rm th}$ is the thermal resistance of the heat flow path. For a thin slab of area A the distance the heat must diffuse is approximately its thickness (d). In this case, $R_{\rm th} = d\rho / ALT$, where $L = 2.2\times 10^{-8}$ W Ω/K^2 is the Lorentz number for K, ρ is the electrical resistivity, T is the temperature, and $R_{\rm th}$ has been related to ρ using the Wiedmann-Franz law. The low-temperature (electronic) heat capacity of the slab is $C = \gamma T d A$, with $\gamma \simeq 4.5\times 10^{-5}$ J/(cm^3 K^2) for potassium. It then follows that $\tau_{\rm th} = d^2 \rho(300\ {\rm K})\gamma / Lr$, where r is the room temperature to low-temperature resistivity ratio. If we substitute $d = 0.05$ cm (our slab thickness), $\rho(300\ {\rm K}) = 6\times 10^{-6}$ Ω cm, and the very conservative estimate $r \geq 10$, the value $\tau \leq 3$ μs is obtained. This time is much less than the FID lifetime, so that in estimating the transient temperature rise due to each pulse, we can use the heat capacity of the entire sample and not just that of the skin depth.

The next step is to estimate the heat energy per pulse (δE) generated by the eddy currents in the skin depth of each layer of the sample. From elementary considerations, it is seen that the instantaneous power associated with the rf pulse (P) in m slabs is

$$P = \frac{\delta E}{\tau} = B H_1^2 A m = \frac{B\theta^2 A m}{\gamma_n^2 \tau^2} = \langle P \rangle \frac{1}{\tau R}, \quad B = \frac{\langle P \rangle \gamma_n^2 \tau}{R\theta^2 A m} \tag{3}$$

where H_1 is the amplitude of the applied rf magnetic field, γ_n is the nuclear gyromagnetic ratio, θ is the pulse nutation angle, τ is the pulse duration, $\langle P \rangle$ is the long-time average power, R is the pulse repetition rate, and B is a factor that depends on the shape and resistivity of the sample, the coil configuration, etc. When the pulses are applied, one effect of $\langle P \rangle$ is to raise the temperature of the mixing chamber. The value of $\langle P \rangle$ for this set of conditions is measured independently by noting the amount of dc power added to the mixing chamber heater that gives the same rise in the steady-state operating temperatures as the rf pulses. The constant B is then determined with a measurement of the ^{27}Al calibrator resonance, where it is easy to identify a 90° pulse. For the conditions of our experiment, $B \simeq 1.4\times 10^{-2}$ W Oe^{-2} cm^{-2}.

Once B has been determined, we have

$$\frac{\delta T}{T} = \frac{\delta E}{CT} = \frac{B}{\gamma_n^2} \frac{\theta^2}{\tau} \frac{1}{\gamma T^2 d} \ . \tag{4}$$

From Eq. (4) it is seen that the fractional temperature rise due to a single pulse can be kept small by using a long value of τ and a small tipping angle. A practical upper limit on τ is either the FID lifetime T_2^* or the longest transmitter pulse the spectrometer will generate. In this

experiment, the latter condition dictated $\tau \leq 120$ μs for our transmitter, which is smaller than T_2^* for the FID of the ^{39}K signal. It is also seen that a progressively smaller factor (θ^2/τ) is needed as the temperature is lowered.

After determining B and taking account of the other parameters that applied to our experiment, the condition $\delta T \leq 10$ mK required $\theta \simeq 0.01$ rad at our lowest temperature. Although this temperature rise was acceptable in our measurements, the small value of θ greatly reduced the signal from a single FID, so that it was necessary to average many times to obtain a satisfactory signal-to-noise ratio.

The optimum repetition rate was determined using the following considerations. From the Bloch equations, one can show that small angle pulses applied at a rate R much greater than the spin-lattice relaxation rate $1/T_1$ will reduce the magnetic moment from its equilibrium value M_0 to

$$M = \frac{2M_0}{2+\theta^2 T_1 R} . \tag{5}$$

Under these conditions, the steady-state FID signal amplitude (S) is $S \propto M \sin\theta \simeq M\theta$. Over a time (t) the number of signals averaged is $n = Rt$. During the same time a noise voltage (N) is accumulated with the property $N \propto n^{1/2}$. It then follows that

$$\frac{S}{N} \propto \frac{M_0(\theta^2 R t)^{1/2}}{2+\theta^2 T_1 R} . \tag{6}$$

The optimum value for S/N is then obtained by setting $\theta^2 R = 2/T_1$, and is independent of θ. Although this condition suggests that a larger θ can be balanced by a smaller R, it must be recognized that the maximum θ is limited by Eq. (4) and that the maximum R must be several times smaller than the spin-phase memory relaxation rate $1/T_2$ in order to avoid repetitive pulse distortion effects in the shape of the FID. The latter condition limits R to values much less than 300 s^{-1} in K. Our experimental measurements of the line shape were done at $R = 30$ s^{-1} for the lowest temperatures investigated.

Because of the possibility that the sample surface would become oxidized in handling, it was important to check that the observed signal was from metallic K. This step was done by measuring T_1 and the Knight shift during the experiment. Rough measurements of T_1 were made over the temperature range 50–100 mK, and a Korringa behavior with $T_1 T = 30 \pm 10$ K s was found. At 1 K, the Knight shift was measured to be $0.24 \pm 0.01\%$. Both measurements agree with results found earlier[10,14] at higher temperatures and identify the nuclei of our experiments as ^{39}K in the metallic state.

Finally, to prevent the static magnetic field from drifting during signal averaging, a different NMR signal (^{27}Al) from a sample outside the cryostat was used to regulate the field.

C. Signal collection and processing

The free-induction decay was recorded on a 1170 Nicolet signal averager. An example is shown in Fig. 1, where the ^{39}K signal at 75 mK is represented by 1024 points. A digital Fourier transform was performed on this to obtain the potassium spectrum. Figure 2(a) shows the low-frequency components of this transform after an adjustment of the phase to obtain the absorption spectrum was made. The large components at very low frequencies on the left-hand side of Fig. 2(a), caused by baseline drift, were removed before an inverse digital Fourier transform was performed. Finally, to improve spectral resolution and avoid the effects of signal truncation, a decaying sinusoid fitted to the free-induction decay was used to extend it to 4096 points. The spectrum enhanced by these techniques is shown in Fig. 2(b).

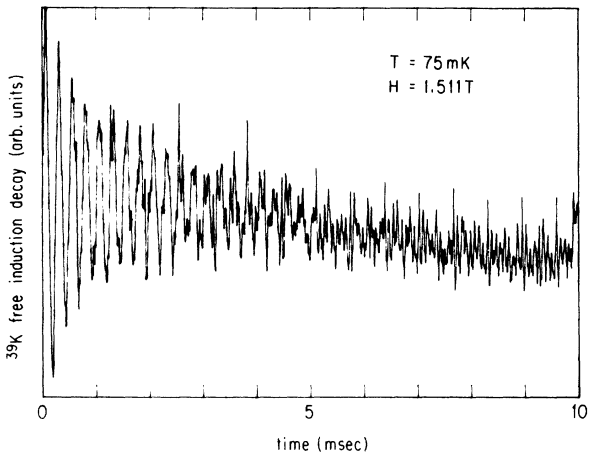

FIG. 1. The free-induction decay of potassium at 75 mK, as recorded on 1024 channels of a 1170 Nicolet signal averager.

The sum of two Lorentzians was fitted to the portion of the spectrum shown. The broad Lorentzian had a half width at half maximum of approximately 3 Oe at all temperatures measured. This type of behavior can be expected for a sample in which electric field gradients caused by impurities produce a quadrupolar broadening.

III. DISCUSSION

In this section we discuss what is indicated by our experimental results with respect to the presence of CDW in K. Our presentation focuses on the narrow component of the ^{39}K line only, as it provides the more sensitive test of the models. The half-width at half maximum of the narrow Lorentzian observed in the spectrum is plotted versus temperature in Fig. 3. We observe a temperature-independent linewidth of 0.294 ± 0.015 Oe from 59 to 420 mK, indicated by the horizontal solid line. Also shown are predictions by Wang and Overhauser.[5] Parameters used in all of these predictions include the phason velocity perpendicular to the CDW direction (1.4×10^5 cm/s), the lattice displacement amplitude (0.03 Å), the phason cutoff frequency (corresponding to 3 K), the CDW wave vector (1.7×10^8 cm^{-1}), and the CDW energy gap (0.62 eV). Different models of phason anisotropy account for the four predictions shown. They are the following.

Case A: Isotropic velocity and isotropic damping.

Case B: Isotropic velocity and anisotropic damping.

Case C: Anisotropic velocity and isotropic damping.

Case D: Anisotropic velocity and anisotropic damping. The anisotropic spectrum forms constant energy surfaces of oblate spheroids, with the axis lengths differing by a factor of 8. For anisotropic damping, the phason lifetime is proportional to $1/\cos^2\phi$, where ϕ is the angle between the phason and CDW wave vector. The details of these models are described in their paper. Subsequent predictions,[6] based on neutron diffraction data[9] which indicate constant energy surfaces of prolate spheroids, cause a linewidth broadening that begins at lower temperatures than those shown.

The linewidth δH due to a static CDW depends on the CDW fractional amplitude, which Wang and Overhauser estimate to be 0.11. With this value, the ^{39}K NMR spectrum in a 1.5-T field would have $\delta H = 4.25$ Oe. Motional narrowing by phasons would reduce this width to approximately[15]

$$\Delta H = \gamma_n (\delta H)^2 \tau_c \ , \tag{7}$$

where τ_c is the correlation time of the hyperfine field due to the phasons. A conservative criterion for the observation of CDW broadening is $\Delta H = 0.2$ G, since a larger ΔH would produce a linewidth clearly larger than the temperature-independent value observed with this sample. This value then sets a limit $\tau_c \leq 8\times 10^{-6}$ s in conjunction with the other parameters listed above. It is to be emphasized that the models used by Wang and Overhauser are representations of very general phason properties that are not well understood. On the basis of our results we conclude that there is no evidence of phasons with correlation times greater than 8×10^{-6} s at temperatures above 60 mK.

If the observed linewidth is not due to a CDW, then other mechanisms may be examined to explain the linewidth. The Van Vleck second moment M_2 due to the nuclear dipolar interaction has been reported as $M_2 = 7700$ (rad/s)^2 in potassium by Follsteadt and Slichter.[11] It indicates a dipolar width $M_2^{1/2}/\gamma_n \simeq 0.07$ G, which is substantially less than the width observed for our sample. It is not clear what is responsible for the linewidth of our sample. Possible mechanisms include the quadrupolar effect of impurities, or perhaps a martensitic transition by part of the sample.[16] For the purpose of this paper, the exact origin of the linewidth is not important, so we do not discuss it further.

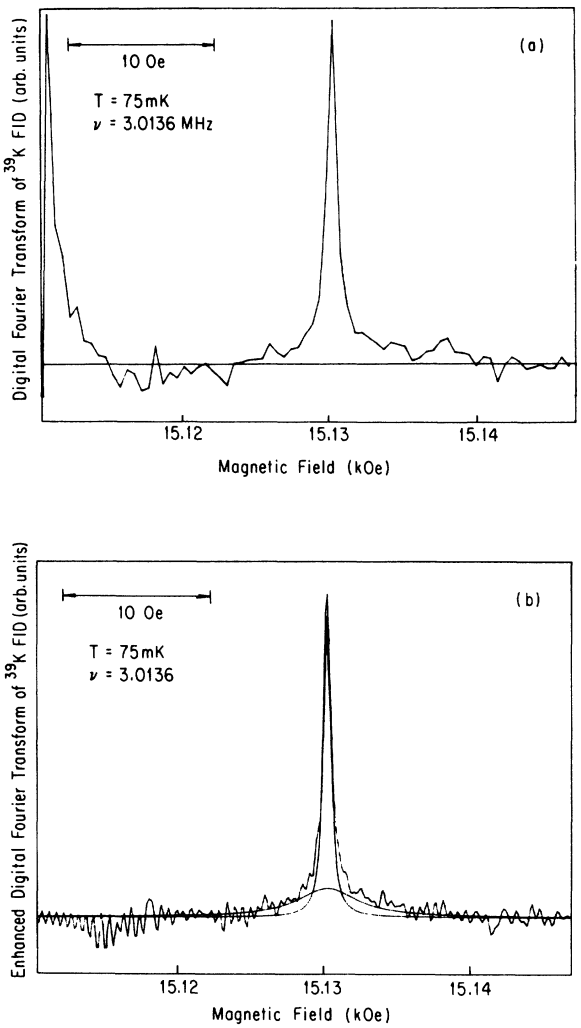

FIG. 2. (a) The digital Fourier transform of the free-induction decay, multiplied by a phase factor to obtain a symmetrical signal. The lowest 75 components of the transform are plotted, showing the large low-frequency components, and the potassium spectrum. (b) Spectrum enhanced by removal of low- and high-frequency components, and by using a decaying sinusoid of best fit to extend the free-induction decay to 4096 points. Also shown in the figure are the two Lorentzians whose sum is the best fit to the spectrum.

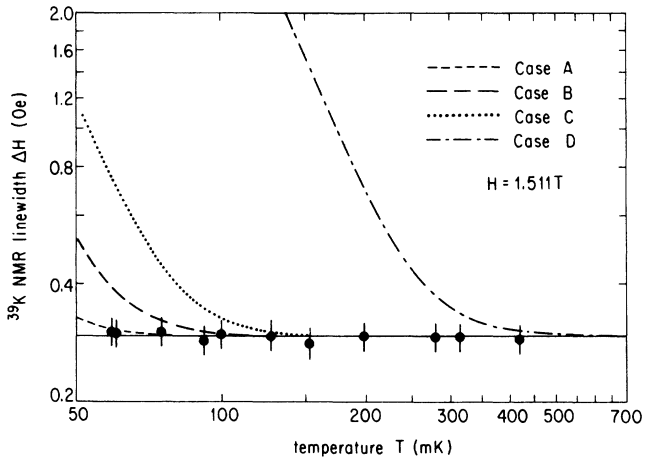

FIG. 3. Temperature dependence of the NMR linewidth in potassium, measured at 3 MHz. The solid line is the temperature-independent linewidth observed (0.294±0.015 Oe). The dashed and dotted lines are predictions for linewidth broadening due to CDW made by Wang and Overhauser (Ref. 5). They are the following. Case A: Isotropic velocity and isotropic damping. Case B: Isotropic velocity and anisotropic damping. Case C: Anisotropic velocity and isotropic damping. Case D: Anisotropic velocity and anisotropic damping. More recent predictions by Wang and Overhauser (Ref. 6), based on neutron diffraction data (Ref. 9), would not display linewidth broadening over the temperatures shown.

IV. CONCLUSIONS

The NMR linewidth for potassium metal is reported at a field of 1.5 T over the temperature range 59–420 mK. A broad and a narrow component are observed, with the narrow one having a half width at half maximum that is 0.294 ± 0.015 Oe over the entire temperature range. This result places restrictions on the properties of the CDW's that have been proposed to form at low temperatures in potassium. In particular, if phasons narrow the linewidth through Knight shift fluctuations, their correlation time must be less than 8×10^{-6} s. This result does not support modes that assign large anisotropies to the CDW phason lifetime or spectrum, as in the first predictions of Wang and Overhauser. Their more recent predictions, based upon a phason spectrum derived from neutron diffraction data, lead to effects that occur at temperatures below what was covered in this work. In order to test their revised parameters, experiments at substantially lower temperatures and preferably at higher magnetic fields are needed.

The critical problem of transient heating of the sample at very low temperatures by the pulsed rf field used for the NMR measurement is analyzed. An experimental method to evaluate it is presented, along with related considerations of obtaining an optimal signal-to-noise ratio.

Measurement of the spin-lattice relaxation time indicates a Korringa constant $T_1T=30\pm10$ s K over the range 50–100 mK. The Knight shift was measured to be $0.24\pm0.01\%$ at 1 K.

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