Polarization of the spin-density waves in lead

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Experimental evidence that shows that lead has 12 small-amplitude spin-density waves (SDW's) with commensurate wave vectors $\mathbf{Q}_i=\{210\}$ is reviewed. An unresolved question has been the polarization direction of the SDW's. Neutron-diffraction satellites from an *s*-band conduction-electron SDW occur only at $\pm\mathbf{Q}$. The fractional modulation of each SDW is ~ 0.01, a value derived from the observed 10^5-fold enhancement in the electronic specific heat at 0.5 K. Neutron-diffraction satellites at $\{210\}$ will then have intensities $\sim 3\times 10^{-5}$ times that of a (nuclear) Bragg reflection provided the (linear) SDW's have transverse polarization. SDW satellite intensities will be zero if the SDW's are longitudinally polarized. Measurements using a highly filtered neutron beam at NIST's BT-9 spectrometer on a pure lead crystal at 4.2 K revealed no (210) satellite at the 5×10^{-8} level. Consequently, one may conclude that the SDW's in lead are longitudinally polarized.

I. BACKGROUND

The purpose of this work is to report an experiment which indicates that the spin-density waves (SDW's) in lead are longitudinally polarized. We will describe below six prior experiments which show that the conduction-electron ground state of Pb has a (static) spin polarization,

$$\mathbf{P}(\mathbf{r})=np\sum_{i=1}^{12}\hat{\boldsymbol{\epsilon}}_i\sin\mathbf{Q}_i\cdot\mathbf{r}\ , \tag{1}$$

where $\{\mathbf{Q}_i\}$, in $2\pi/a$ units, are the 12 commensurate $\{210\}$ vectors in reciprocal space, and $\{\hat{\boldsymbol{\epsilon}}_i\}$ are their corresponding unit polarization vectors. The fractional amplitude p of each SDW, relative to the mean conduction electron density ($n=4$ per atom), is ~ 0.01. (This value is derived from the size of the anomalous specific heat in the superconducting state.) The directions of the polarization vectors $\{\hat{\boldsymbol{\epsilon}}_i\}$ have remained undetermined until now.

SDW instability of a Fermi liquid caused by arbitrary repulsive interactions was first derived in one dimension.[1] Subsequently a similar proof for a degenerate electron gas in three dimensions, within the Hartree-Fock approximation, was demonstrated.[2] The SDW instability theorem is valid even for high electron densities. The first application involving an elemental metal was to chromium,[2] which has an incommensurate, linear SDW with $\mathbf{Q}$ parallel to one cubic axis. The polarization $\hat{\boldsymbol{\epsilon}}$ is longitudinal for $T<123$ K and transverse for $T>123$ K. Studies of SDW antiferromagnetism in Cr are extensive.[3] Observation of the magnetic satellites in Cr by neutron diffraction is easy because the SDW amplitude (associated with Cr's *d* band) is 0.6 Bohr magneton per atom. A magnetic satellite in Cr is $\sim 20\%$ of a (nuclear) Bragg reflection.

The neutron-scattering length of an electron spin S is, in general, given by[4]

$$b_M=0.54\times 10^{-12}Sf\ \text{cm}\ , \tag{2}$$

where f is the magnetic form factor. For a sinusoidal wave, as in Eq. (1), $f=\frac{1}{2}$ and $S=\frac{1}{2}$. Accordingly, with four conduction electrons per atom and a fractional modulation of 0.01, the equivalent magnetic scattering length is

$$b_M=5.4\times 10^{-15}\ \text{cm}\ . \tag{3}$$

Since the nuclear scattering length of Pb is $b=0.94\times 10^{-12}$ cm, the relative intensity of a *transverse* SDW satellite compared to a Bragg reflection is $(b_M/b)^2$, i.e.,

$$I_{\text{SDW}}/I_G=3\times 10^{-5}\ . \tag{4}$$

A magnetic satellite having this relative intensity can be observed readily.

If a sinusoidal SDW has *longitudinal* polarization, the SDW satellite intensity will be zero. The reason for this null result can be understood simply. The interaction energy of a neutron magnetic moment $\boldsymbol{\mu}_N$ with its magnetic environment is $-\boldsymbol{\mu}_N\cdot\mathbf{B}(\mathbf{r})$, where $\mathbf{B}(\mathbf{r})$ is the magnetic induction at the position $\mathbf{r}$ of the neutron. Now,

$$\text{curl}\mathbf{B}=\frac{4\pi}{c}\mathbf{j}\ , \tag{5}$$

where $\mathbf{j}(\mathbf{r})$ is the Amperian-current distribution associated with the magnetization $\mathbf{M}(\mathbf{r})$, i.e.,

$$\mathbf{j}=c\ \text{curl}\mathbf{M}\ . \tag{6}$$

However, for a longitudinally polarized SDW,

$$\mathbf{M}=np\mu_B\hat{\boldsymbol{\epsilon}}\sin\mathbf{Q}\cdot\mathbf{r}\ , \tag{7}$$

where μ_B is the Bohr magneton and $\hat{\boldsymbol{\epsilon}}$ is parallel to $\mathbf{Q}$. It follows from the parallelism that $\text{curl}\mathbf{M}=0$; whereupon

from (5) and (6), curl$\mathbf{B}=0$. Since also div$\mathbf{B}=0$, then $\mathbf{B}\equiv 0$. Accordingly a neutron has no interaction with a longitudinal SDW; so the relative intensity of the SDW satellite will be

$$I_{\mathrm{SDW}}/I_G=0\ . \tag{8}$$

The foregoing argument followed from the assumption that the conduction electrons are nearly free. That is to say, the Fourier components ρ_G of their charge density (for reciprocal-lattice vectors $\mathbf{G}\neq 0$) are small. Pb is a nearly free-electron metal; its Fermi-surface deviations from an ideal sphere are slight (when viewed in the extended zone scheme).[5] It follows that SDW satellites at $\mathbf{G}\pm\mathbf{Q}$, for which $\mathbf{G}\neq 0$, will have very little intensity, regardless of polarization. The final conclusion is that neutron-diffraction satellites caused by the SDW's in Pb can be readily observed, viz., Eq. (4), if $\hat{\boldsymbol{\epsilon}}$ is transverse to $\mathbf{Q}$; but they should be invisible if $\hat{\boldsymbol{\epsilon}}$ is parallel to $\mathbf{Q}$.

II. EXPERIMENTAL DETAILS AND RESULTS

The Pb single crystal (six 9*s* purity) was obtained from Metal Crystals & Oxides, Ltd., Cambridge, U.K. It was a cylinder 3 cm in diameter and 6 cm long. The axis was [001]. The (200) rocking curve was symmetric, had no structure, and was 0.3° wide. The Pb crystal was cooled to 4.2 K in a fixed temperature cryostat. The BT-9 spectrometer at the National Institute of Standards and Technology was equipped with a pyrolytic-graphite (002) monochrometer and analyzer. λ was 2.43 Å. The Soller collimators were 40′,40′,40′,40′; and energy resolution was 0.8 meV.

Pb is face-centered cubic; so only half of the (hkl) points in reciprocal space are reciprocal-lattice vectors, i.e., those for which h,k,l are either all odd or all even. The remaining (hkl) points, e.g., (100), (110), (210), (211), etc., are superlattice points and will exhibit no reflection if the neutron beam is pure (100% λ). Contamination of the beam by $\lambda/2$ neutrons, a natural feature caused by a crystal monochrometer, will lead to fictitious λ "satellites" at (100), (110), etc., since all spectrometer settings (in the elastic mode) will be identical to $\lambda/2$ Bragg reflections from (200), (220), etc.

The dominant problem, therefore, was removal of $\lambda/2$, $\lambda/4$, etc., neutrons from the beam. Three graphite filters were used: 2.5″ at the entrance of collimator no. 2, 2.5″ at the entrance of collimator no. 3, and 1″ at the exit of collimator no. 2. Without the last filter there was an elastic (110) peak, caused by $\lambda/2$ neutrons diffracting from (220), having intensity $\sim 1\times 10^{-6}$ of the (200) Bragg peak. With all three filters, no peak was visible to 5×10^{-8}, the level of statistical noise (for 40-min counting times), relative to the (200) Bragg peak, which was 2×10^{8} counts (corrected for counter saturation).

A high-sensitivity, longitudinal, elastic scan was made through the (210) point which, as outlined in the following section, is a SDW satellite point for Pb's electronic ground state, given by Eq. (1). There was no detectable (210) peak at the 5×10^{-8} sensitivity level, i.e., 600 times smaller than the value, Eq. (4), anticipated for a transversely polarized SDW. One may conclude that the SDW's in Pb are longitudinally polarized, so that Eq. (8) is the correct alternative for the intensity of the magnetic satellites.

III. EVIDENCE FOR THE SDW STRUCTURE OF Pb

It is necessary to recapitulate the experimental facts which manifest the SDW broken symmetry, described by Eq. (1), in order to forestall the possibility that the null result just described might be viewed as indicating absence of any magnetic structure. Six phenomena will be reviewed.

(1) Phonon spectrum. Thirty years ago Brockhouse *et al.*[6] discovered that Pb's phonon frequencies (longitudinal and transverse) had large dips, $\sim 30\%$, at the $\{100\}$ zone boundary points. Many conventional attempts to explain this behavior were made, but none were successful. A recent study[7] has reinforced the conclusion that these dips are truly pathological.

A quantitative theory[8] of the influence of SDW's on lattice dynamics was successful in explaining these pathological dips at the $\{100\}$ points. SDW's create an additional conduction-electron charge response caused by an induced phase slip of an up-spin (i.e., parallel to $\hat{\boldsymbol{\epsilon}}$) density modulation relative to a down-spin modulation.[8] The experimental behavior requires a full cubic family of small-amplitude $\{210\}$ SDW's. Precise commensurability of the $\mathbf{Q}$'s with the $\{210\}$ points was not required. (At most a 2% deviation could be tolerated.) However, the nuclear magnetic resonance linewidth demands that the $\mathbf{Q}$'s be *exactly* commensurate since, then, all 12 of the SDW's have nodes at the nuclear sites. Were this not the case, the spin polarization of the SDW's would cause a broad spectrum of hyperfine fields (at the Pb nuclei) having magnitudes $\sim 10^{5}$ G. In fact, the observed NMR linewidth, for a measurement field of 9.5 kG, is only ~ 1.6 G.[9]

(2) Electronic specific heat in the superconducting state. The electronic heat capacity of a superconductor (below T_c) should fall off as $\exp(-\Delta/k_BT)$ with decreasing temperature. This behavior is observed in many metals. However, for Pb, there is a low-temperature tail that is quite extraordinary.[10] At 0.5 K the electronic specific heat is too large by 10^{5}, when compared with the expected value for a strong-coupling superconductor having $2\Delta=4.2k_BT_c$.

This 5 order-of-magnitude discrepancy can be explained by the presence of SDW's. The superconducting gap parameter $\Delta(\mathbf{k})$ is driven to zero (or near zero) when $\mathbf{k}$ is near the energy gaps created by the SDW's.[11] Consequently, there are always regions on the Fermi surface where $\Delta(\mathbf{k})$ is very small, so that thermal excitations across the superconducting gap can more easily occur. The low-temperature tail is a power law ($\sim T^2$) instead of an exponential. Gap anisotropy caused by Fermi-surface or phonon anisotropy is much too small[12,13] to alter the exponential decrease predicted by standard theory.[14]

A fit of the SDW-induced T^2 tail to experiment[11] leads to SDW energy gaps ~ 0.2 eV, which is a measure of the SDW exchange potential.[1] The fractional spin polarization of each SDW is, accordingly, $p\sim 0.01$. The 0.2-eV

SDW gaps imply that the SDW structure is present at all temperatures below the melting point of Pb (600 K), since the ratio between the SDW transition temperature and SDW energy gap is similar to that for superconductivity.[2]

Finally, it is important to remember that Pb is the exemplar of singlet-pairing superconductors. For it was on Pb that the coherence factors of the Bardeen-Cooper-Schrieffer theory[15] were first evident experimentally,[16,17] and for which the image of the phonon spectrum was first observed in tunneling spectra.[18,19] Nevertheless, 30 years have elapsed since the discovery[20] of the specific-heat tail which, at 0.5 K, reveals an equilibrium thermodynamic discrepancy of 10^5. The SDW structure given by Eq. (1) is the only explanation so far advanced.

(3) Ultrasonic attenuation in the superconducting state. Below T_c the ultrasonic attenuation caused by electronic transitions should fall to zero with decreasing temperature as $\exp(-\Delta/k_B T)$, similar to the behavior of the specific heat.[15] This temperature dependence has been verified in Sn and In,[21] as well as in other superconductors. However, in Pb there is an anomalous low-temperature tail[22] having the same discrepant behavior as the specific-heat anomaly. Since the attenuation data extend only to 1.8 K, the maximum discrepancy is a factor of 40 (which is comparable to the specific-heat anomaly at that temperature).

Electronic transitions that cause attenuation of a longitudinal wave along $\hat{\mathbf{x}}$ occur only near the $\hat{\mathbf{y}}\hat{\mathbf{z}}$ equatorial plane of the Fermi surface. Energy gaps arising from the $\{210\}$ SDW's intersect this plane is 16 places. A quantitative theory of the SDW-caused attenuation provides an explanation of the anomalous behavior.[23] It should be noticed that a $\{211\}$ family of SDW's could not explain this phenomenon since none of the SDW energy gaps would intersect the $\hat{\mathbf{y}}\hat{\mathbf{z}}$ plane. (A $\{211\}$ SDW family was considered to be a possible, but less satisfactory alternative to a $\{210\}$) family in connection with the phonon spectrum.[8])

(4) Normal-insulator-superconductor tunneling. Electrons having velocity perpendicular to the face of a tunneling structure are the ones that dominate the conductance. Ordinarily a Pb film will have its (111), close-packed planes parallel to the surface. Accordingly, the electrons which dominate the conductance will be ones having velocity near the [111] direction. SDW energy gaps from the $\{210\}$ family do not come near to the [111] direction of Pb's Fermi surface where, in the superconducting state, the energy gap 2Δ would have its imputed value. Consequently, most tunneling experiments would not be sensitive to the SDW's.

Quench-condensed Pb films are crystalline but not epitaxially textured. Tunneling conductance measurements at 1.1 K on three quench-condensed Pb films revealed a low-bias conductance 0.03 times that for the same structure in the normal state.[24] The relative conductance was expected to be 3×10^{-6}, so the discrepancy is a factor of 10^4. A theory of the SDW enhanced tunneling conductance[25] led to a predicted relative conductance of 0.02, a fortuitously close agreement. There has been no physically based alternative interpretation other than attributing the extra conductance to pin holes in all of the Al_2O_3 layers. However, the anomalous conductance increased *regularly* with additions of Gd solutes to the Pb films.[24] This behavior should be anticipated since paramagnetic solutes will (at low temperature) cause the SDW amplitudes to grow, if already present in the pure metal. (The creation of SDW's by paramagnetic solutes[26] is now well established in dilute alloys[27] by direct observation of magnetic satellites by neutron diffraction.)

(5) Scanning-tunneling-microscope studies of Pb films. Chen *et al.*[28] have exhibited a series of scanning-tunnel-microscope (STM) tunneling spectra on superconducting Pb films. The films were 4000 Å thick and were deposited on [100] Si chips. Tunneling spectra were taken at regular 15, 20, or 30-Å intervals. Boundaries were discovered across which the tunneling spectrum changed from ones having the expected 2.4 meV energy gap to ones that were strictly ohmic. The transition was complete in a 30 Å interval. The coherence length of Pb is 830 Å, so such rapid changes in tunneling spectra should not be possible.

Interpretation of the foregoing behavior is easily made when the SDW structure is recognized. The boundary need only be one between a [111] Pb grain and a [100] grain. (*Both* grains are superconducting.) For reasons given above the [111] grain will exhibit the standard tunneling spectrum with $2\Delta=2.4$ meV. Electrons tunneling in the [100] grain will have velocities close to the [100] direction. However, four $\{210\}$ SDW energy gaps intersect the Fermi surface near a [100] direction; so electrons having [100] velocity directions will be at a Fermi surface location where $\Delta\sim0$. Accordingly an ohmic conductance should occur. (Of course, it would be interesting to confirm the grain orientations on either side of the boundary.)

(6) Muon spin relaxation. In face-centered-cubic metals muons come to rest (at 4 K) in octahedral interstitial sites. These sites, $(\frac{1}{2},0,0)$, etc., are nodes for the 12 $\{210\}$ SDW's; so the muon spin relaxation will be caused by the usual interaction with nuclear dipole moments. The expected relaxation rate for Pb at 4 K is observed and, as a result of thermally activated muon diffusion with increasing temperature, the relaxation rate falls to zero (a consequence of motional narrowing) at 40 K. However, above 60 K, the relaxation rate becomes finite again and increases monotonically up to room temperature.[29]

This behavior can also be understood because the tetrahedral interstitial sites, $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$, etc., are SDW antinodes. The total fractional conduction-electron polarization at each tetrahedral site is $\sim3\%$, so each site will provide a large hyperfine field for a muon which resides there by thermal activation. These hyperfine fields will be severely motionally narrowed, but they are so large to begin with, ~3000 G, that the experimental data can be explained.[30] It should be appreciated that this phenomenon provides direct evidence of exotic magnetic structure.

IV. CONCLUSION

The foregoing review shows that many phenomena in Pb, some of which have been known for 30 years, can for

the first time be understood, and *all* appear to be effects caused by 12 {210} SDW's. The absence of a (210) magnetic satellite therefore implies that the SDW polarizations are longitudinal.

Needless to say, it is of interest to inquire whether Pb's SDW's can be made visible to neutrons by inducing their polarization vectors $\{\hat{\epsilon}_i\}$ to have transverse components. In principle, $\hat{\epsilon}$ can be forced to rotate relative to **Q** by a sufficiently strong magnetic field. The spin susceptibility of a SDW state is anisotropic, and the axis of anisotropy is $\hat{\epsilon}$.[31] The sign of the anisotropy depends on whether $Q/2k_F$ is greater than or less than unity. For Pb, $Q/2k_F=0.90$, which implies that $\chi_{\parallel}<\chi_{\perp}$. The magnitude of the difference is likely only $\sim 0.01\%$ on account of the small SDW amplitude.

Suppose there is an applied field **H** at an angle ψ from **Q**, and let θ be the rotation angle of $\hat{\epsilon}$ from **Q** (in the plane of **Q** and **H**), then the energy change versus θ will be, with $\Delta\chi=\chi_{\parallel}-\chi_{\perp}$,

$$\Delta E=\lambda\sin^2\theta-\tfrac{1}{2}\Delta\chi H^2\cos^2(\psi-\theta)\ . \tag{9}$$

λ is the (unknown) parameter describing the uniaxial anisotropy causing $\hat{\epsilon}$ to be parallel to **Q**. On letting $\theta<1$ and assuming that $\Delta\chi H^2<\lambda$, one finds that the optimum orientation of **H** is 45° and that the rotation of $\hat{\epsilon}$ is

$$\theta=\frac{\Delta\chi H^2}{4\lambda}\ . \tag{10}$$

The physical origin of λ will involve spin-orbit coupling and the periodic potential of the crystal. Predicting the size of λ is clearly a formidable problem. A rotation angle $\theta>0.1$ rad will be required to generate a clear magnetic satellite. With increasing H below high-field saturation, the intensity of an induced magnetic satellite will be proportional to H^4. A successful experiment will probably require a spectrometer equipped with a superconducting magnet that can be oriented at a 45° angle from the scattering vector.

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