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Theory of charge-density-wave–spin-density-wave mixing

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Metals with a charge-density-wave broken symmetry will acquire a spin-density-wave component if the charge-density-wave amplitude is sufficiently large and if the elastic stiffness constants are sufficiently anharmonic. This effect has implications for the compatibility of charge-density waves with superconductivity.

The spin-up and spin-down electron densities of a metal having a broken translational symmetry are¹

$$\begin{aligned} \rho^+(\vec{r}) &= \frac{1}{2}\rho_0[1 + p \cos(\vec{Q} \cdot \vec{r} + \phi)] , \\ \rho^-(\vec{r}) &= \frac{1}{2}\rho_0[1 + p \cos(\vec{Q} \cdot \vec{r} - \phi)] . \end{aligned} \tag{1}$$

The wave vector and fractional amplitude of the wave are \vec{Q} and p ; $\rho_0(\vec{r})$ is the conduction electron density (having the periodicity of the lattice) which would otherwise prevail. The “spin-split-phase” angle ϕ describes the degree of charge-density-wave–spin-density-wave (CDW-SDW) mixing. If $\phi = 0$, Eq. (1) describes a pure CDW; if $\phi = \frac{1}{2}\pi$, it describes a pure SDW. In this paper I investigate the conditions which would allow ϕ to have an intermediate value.

Broken translational symmetry in two- or three-dimensional metals is caused by exchange and correlation contributions to the conduction electron energy.^{1,2} The purely electronic energy relative to the normal state ($p = 0$) can be described approximately:

$$\Delta E_e \approx \epsilon_0 - \alpha p^2 + \beta p^4 + p^2 D \sin^2 \phi . \tag{2}$$

The coefficients α and β describe a parabolic minimum which determines p^2 (provided $\Delta E_e < 0$). The constant ϵ_0 has been included to emphasize the fact that Eq. (2) is not valid for $p \sim 0$. The reasons for this stem from the correlation energy correction,¹ and are related to the conclusion that a CDW instability can be a first-order, rather than a second-order, transition.³

The last term of Eq. (2) describes the dependence of the correlation energy on the spin-split phase ϕ . Since the correlation energy arises primarily from virtual scattering of antiparallel-spin electrons, it favors a CDW instead of an SDW because the scattering matrix elements are enhanced when the crests in the spin-up and spin-down charge modulations coincide (in real space).¹

The ordinary Coulomb energy prohibits a CDW instability unless a periodic lattice displacement $\vec{u}(\vec{r})$ of the positive-ion lattice compensates the charge modulation, i.e.,

$$\vec{u} = \vec{A} \sin(\vec{Q} \cdot \vec{r}) . \tag{3}$$

Local charge neutrality requires that the amplitude \vec{A} satisfy

$$z |\vec{A} \cdot \vec{Q}| = p \cos \phi , \tag{4}$$

where z is the effective charge of the ion for the wave vector \vec{Q} . For example, if Z is the nuclear charge of a monovalent metal, then $z = Z - (Z - 1)f(Q)$, where $f(Q)$ is the x-ray form factor.⁴ The directions of \vec{Q} and \vec{A} depend on the anisotropy of the elastic stiffness constants.⁵

Elastic-stress energy is therefore an important energy contribution which impedes a CDW instability. It will be

$$\Delta E_s = \lambda p^2 \cos^2 \phi + \mu p^4 \cos^4 \phi , \tag{5}$$

where λ is proportional to the elastic stiffness (for the directions of \vec{Q} and \vec{A}), and μ is a coefficient proportional to the anharmonic correction. The condensation energy of a mixed CDW-SDW is accordingly

$$\Delta E = \Delta E_e + \Delta E_s . \tag{6}$$

It is clear that a large elastic-stress term favors a SDW, whereas the spin-split-phase term of (2) favors a CDW. For small p , a pure CDW or SDW occurs depending on whether $D > \lambda$ or $D < \lambda$. The conclusion that Na and K have CDW states,^{3,6} whereas Cr has a SDW state,² should not be thought surprising since the elastic constants of Na and K are two orders of magnitude smaller than those of Cr.

Minimization of the total condensation energy, Eq. (6), leads to

$$p^2 = \frac{\alpha - D \sin^2 \phi - \lambda \cos^2 \phi}{2(\beta + \mu \cos^4 \phi)} . \tag{7}$$

This solution to the variational problem applies only if the numerator is positive, otherwise $p = 0$. Further variation of ΔE with respect to ϕ , after substitution of Eq. (7) for p^2 in ΔE , leads to the optimum amount of CDW-SDW mixing. I first obtain

$$\Delta E = \epsilon_0 = \frac{(\alpha - D \sin^2 \phi - \lambda \cos^2 \phi)^2}{4(\beta + \mu \cos^4 \phi)} . \tag{8}$$

The equilibrium value of ϕ is then given by

$$\cos^2\phi = \frac{\beta(D-\lambda)}{\mu(\alpha-D)} \quad (9)$$

As noted above, one obtains a pure SDW if $D < \lambda$, so that Eq. (9) is pertinent only when $D > \lambda$. In this latter case only a pure CDW can occur if $D > \alpha$. Equation (9) can be applied only when all of its factors are positive. A SDW component occurs if (9) is less than unity, i.e.,

$$\mu > \frac{\beta(D-\lambda)}{(\alpha-D)} \quad (10)$$

In order to perceive the trends which lead to CDW-SDW mixing one may neglect λ in comparison to D and D in comparison to α . The criterion, Eq. (10), reduces to a crude but instructive one:

$$\mu > \frac{\beta D}{\alpha} \text{ or } \mu p^2 > \frac{1}{2} D \quad (11)$$

The second alternative follows from the relation $p^2 \sim \alpha/2\beta$, obtained from the leading terms of Eq. (7). Thus the criterion for a SDW admixture is more easily satisfied if the CDW amplitude p and the anharmonic coefficient μ are both large. This is easily understood: Suppose that α (the driving force of the instability) is slowly increased. The anharmonic term $\mu p^4 \cos^4\phi$ gradually dictates a preference for further growth in p through a SDW component (which requires no further lattice strain). Only the correlation energy $Dp^2 \sin^2\phi$ intervenes to effect a compromise. Equation (10) shows that CDW-SDW mixing can occur only when anharmonic elastic effects are included.

Experimental detection of a mixed CDW-SDW requires the juxtaposition of satellite intensity measurements from x-ray and neutron scattering. X-rays are scattered primarily by the periodic lattice distortion, Eq. (3). The CDW satellites occur for scattering vectors $\vec{G} \pm \vec{Q}$, where $\{\vec{G}\}$ are the reciprocal-lattice vectors.⁷ On the other hand, neutrons are scattered by both the lattice distortion and by the magnetic field of the SDW component which, from magnetic energy considerations, will likely be polarized perpendicular to \vec{Q} . Since the SDW exists only in the conduction electrons, the magnetic scattering amplitude will be significant primarily for scattering vectors $\pm \vec{Q}$. Accordingly, the signature of a mixed CDW-SDW will be anomalous neutron scattering amplitudes for the two satellites of $\vec{G} = 0$ in comparison to the satellites of other \vec{G} . The difference will be most pronounced for CDW-SDW states of an s - p energy band. In this case the $\pm \vec{Q}$ satellites may have intensities so different from those of other \vec{G} that x-ray measurements may not be

needed. Interesting polarized-beam effects become possible if the SDW polarization vector can be rotated by external fields.⁸

A pure CDW is compatible with superconductivity since the periodic potential caused by the broken symmetry is no different from that of a crystalline periodicity. The electronic density of states at the Fermi energy $N(E_F)$ can be either increased or decreased by the CDW, depending on whether $Q/2k_F$ is greater than or less than unity.¹ The time-reversed partners of amplitude-modulated conduction electrons are still degenerate, so that Cooper pairing is unaffected. However, this is no longer the case for a mixed CDW-SDW state.

The self-consistent periodic potential of a mixed state corresponding to Eq. (1) is

$$V(\vec{r}) = -W[\cos\phi \cos(\vec{Q} \cdot \vec{r}) - \sigma_z \sin\phi \sin(\vec{Q} \cdot \vec{r})] \quad (12)$$

where σ_z is the Pauli spin operator. This potential does not have time-reversal symmetry. If $\psi_{\vec{k}}$ is an up-spin eigenstate of the Schrödinger equation having the potential (12), then $T\psi_{\vec{k}}$ is not an eigenstate. (T = time-reversal operator). Indeed, the energy expectation value of $T\psi_{\vec{k}}$ will differ substantially from that of $\psi_{\vec{k}}$. As a consequence, singlet pairing will be suppressed.

A well-known problem in superconductivity is the absence of superconductivity in Li,⁹ at least down to 6 mK.¹⁰ Calculations of the electron-phonon interaction constant¹¹ indicate a value $\lambda = 0.4$. This would lead to a transition temperature $T_c \sim 1$ K, based on McMillan's formula with $\mu^* = 0.10$. Optical data¹² of metallic Li indicate an anomalous absorption with a threshold $W \sim 1.3$ eV, analogous to the Mayer-El Naby anomaly¹³ in K ($W \sim 0.6$ eV) and the Hietel-Mayer anomaly¹⁴ in Na ($W \sim 1.2$ eV). The open-orbit magnetoresistance spectra¹⁵ of Na and K show the dramatic effects of CDW structure, which also accounts for the optical anomalies.^{16,17} It is known that Li is very anharmonic, even at liquid-helium temperature.¹⁸ I speculate that the absence of superconductivity in Li may be caused by a mixed CDW-SDW state.

Since a CDW can occur only if a periodic lattice distortion, Eq. (3), compensates the charge modulation, reduction (or elimination) of the CDW amplitude p may be achieved by interfering with the ability of ions to undergo displacements easily. Interstitial impurities, radiation damage, or freezing-in an amorphous state might accomplish this.¹⁹ The criterion Eq. (10), for SDW mixing would then be more difficult to satisfy. As a consequence, metals which ought to be superconducting might be enabled to become so.

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