Whether the activity of cyclic CMP phosphodiesterase is also depressed in certain malignant growths, such as in the fast growing Morris hepatoma 3924A, in which we observed depressed activity of cyclic GMP phosphodiesterase and, conversely, increased activity of cyclic AMP phosphodiesterase (*13*), and in leukemia L-1210 cells and myeloid leukemic tumors, remains to be seen. If such is the case, then cyclic CMP phosphodiesterase would represent a new site of bioregulation in the pathologic processes. Substances that inhibit and stimulate the activity of this enzyme would probably be potential carcinogens and anticancer agents, respectively.

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P-State Pairing and the Ferromagnetism of $ZrZn_2$

Abstract. *It is ascertained that, within the range of stability, the transition temperature of the superconducting solutions between Ti and Zr and between Zr and Hf, and the Curie point of the corresponding ferromagnetic solutions between* $TiZn_2$ *and* $ZrZn_2$ *and between* $ZrZn_2$ *and* $HfZn_2$, *follow a parallel behavior. From this correlation it is concluded that the weak itinerant ferromagnetism of* $ZrZn_2$ *must be due to electron-phonon interaction. Theoretical arguments are advanced to show that the underlying mechanism is hindered p-state pairing, due to a strongly localized repulsive part of the pair-potential that acts as a Hubbard interaction and gives rise to a Stoner instability.*

There can be no doubt that, in metallic ferromagnetic compounds in which the individual elements do not show any magnetic ordering of their own, the moment must be due to itinerant electrons. At present only two such compounds are known, $ZrZn_2$ and Sc_3In.

We want to show that, at least in $ZrZn_2$, the ferromagnetism is due to electron-phonon interaction. This conclusion is a consequence of two seemingly uncorrelated experimental facts, never considered together before.

1) The solid solutions between Ti and Zr and between Zr and Hf show one distinct maximum in their superconducting transition temperature T_s, which occurs between Ti and Zr and is accompanied by some softening of the lattice. The maximum T_s exceeds the T_s of pure Ti and Zr by at least a factor of 2, while from Zr to Hf the solution just shows a monotonic decrease of T_s (*1*).

2) In contrast, the solid solutions between $TiZn_2$ and $ZrZn_2$ and between $ZrZn_2$ and $HfZn_2$ show the parallel behavior for their Curie points T_m (*2-4*). The maximum T_m between $ZrZn_2$ and $TiZn_2$ unfortunately coincides roughly with the limit of stability for the cubic Laves phase, *C* 15 (*3*); $TiZn_2$, the hexagonal Laves phase *C* 14, is no longer ferromagnetic. Obviously, mass variation and mode softening are the only crucial factors.

The following mechanism seems to be the only one to account for the seemingly disconnected facts; that is, the dominant part of the Cooper-pair potential is attractive in the elements, leading to superconductivity, while it becomes repulsive in their *C* 15 compounds leading to ferromagnetism. We wish first to give a naive BCS (Bardeen, Cooper, Schrieffer) argument for this hypothesis and its consequences, and come back later to more sophisticated considerations related to strong-coupling superconductivity theory.

In BCS theory, the change of sign of the pair potential can be obtained by assuming the predominance in the elements of a "hard mode" with frequency $\omega_q \gtrsim \omega_0$, ω_0 being the BCS cutoff (*5, 6*), and of a "soft mode" $\omega_q \ll \omega_0$ in the corresponding compounds. The maximum of T_s in the elements then is a consequence of some softening of the hard mode toward ω_0, while the maximum of T_m in the compounds follows from the soft-mode frequency going to zero at the limit of phase stability. These properties are immediate consequences of the form of the Cooper-pair potential (*5*)

$$V_{pp'} = |g_{pp'}|^2 D(p - p', \epsilon_p - \epsilon_{p'})$$

where

$$D(q, \omega) = 2\omega_q/[\omega^2 - (\omega_q - i\delta)^2]$$

is the phonon propagator and $g_{pp'}$ the electron-phonon coupling constant.

In the "soft mode" case of the compounds, the repulsive part of $V_{pp'}$ increasingly dominates as $\omega_{p-p'} \rightarrow 0$. And since for a repulsive pair-interaction the cutoff ω_0 becomes unimportant, $V_{pp'}$ actually extends up to the Fermi wave number, so that its Fourier transform is strongly localized in physical space. For superconductivity this means that *s*-state pairing is strongly inhibited so that *p*- (or higher) state pairing would become essential (*6*). However, the strongly localized Cooper-pair repulsion now acts like a Hubbard interaction, giving rise to a Stoner instability (*7*) and hence to ferromagnetic ordering induced by the electron-phonon interaction and, at the same time, suppressing *p*-state pairing superconductivity. Beyond the structural transformation from *C* 15 to *C* 14 the above effect vanishes. *C* 14, after all, must be considered the link between the cubic *C* 15 phase and the hexagonal close-packed (hcp) elements.

The mass variation going from $TiZn_2$ to $HfZn_2$ (and also from the element Ti to Hf) is another indication of the electron-phonon origin of the magnetic ordering since it is easily explained by the mass-dependence of the mode frequencies and of the electron-phonon coupling constant,

$$|g_{p,p'}|^2 \omega_{p-p'} \propto M^{-1}$$

The above naive explanation is actually confirmed by a more elaborate analysis in terms of strong coupling su-

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perconductivity theory (*8*). On the one hand, the attractive pair potential in the elements corresponds to the usual positive λ (*9*), and the correlation between the maximum T_s and softening (hard) modes is easily explained by the McMillan form (*8, 9*)

$$\lambda = C/\langle\omega^2\rangle \cdot M$$

On the other hand, the repulsive effect of a soft mode in the compounds is in agreement with Allen's investigation of this problem (*10*). However, since we are interested in the disappearance of superconductivity, the conditions of interest here are $T_s \sim \omega_q \ll \omega_0$, for which Allen's λ_a may become slightly negative. This conclusion is also supported by the more general analysis of Bergmann and Rainer (*11*). Indeed, for $T_s \ll \omega$ the change of T_s due to a spectral variation becomes inversely proportional to ω, $\delta T_s/\delta\alpha^2F(\omega) \propto \omega^{-1}$, which shows that, in the case $T_s \rightarrow 0$, the low-frequency part of $\alpha^2F(\omega)$ determines T_s. And since the Coulomb pseudo-potential μ^* becomes relatively more important, a change of sign of $\delta T_s/\delta\alpha^2F(\omega)$ cannot be excluded either.

The last point of our more elaborate analysis concerns the possibility of an electron-phonon induced Stoner instability. If $I_{(\mathrm{el-ph})}\,\chi^0\,(p, \omega; k, \nu)$ designates the iteration step in the electron-hole t-matrix (*7, 12*) due to phonon exchange, the contribution to the Stoner factor, averaged over the Fermi surface S_F, is given by

$$I_{(\mathrm{el-ph})}N(0) \equiv \langle I_{(\mathrm{el-ph})}\chi^0(p, p; 0, 0)\rangle_{S_F} =$$

$$2\int d\omega\alpha^2F(\omega) \times$$

$$\left[\frac{1}{\omega} - \frac{1}{E_B - \omega} - \frac{\omega}{(\omega - i\delta)^2}\right]$$

Neglecting the bandwidth ($E_B \rightarrow \infty$), assuming a dominant soft and overdamped phonon, so that the imaginary part, δ, of the phonon self-energy exceeds the renormalized frequency ω, then $I_{(\mathrm{el-ph})}N(0) \cong \lambda$. Assuming further that the Coulomb part of the Stoner factor is just too weak to produce the instability we obtain the estimate

$$I_{(\mathrm{el-ph})}N(0) \gtrsim I_{\mathrm{total}}N(0) - 1 \cong 0.5 \times 10^{-4}$$

which is based on the values $T_m \cong 35$ K and $\epsilon_F \cong 0.2$ eV for $ZrZn_2$ (*13*). This shows that λ is probably quite small, of the order of 10^{-4}.

With regard to soft phonons it should be remembered that the most effective contribution to the phonon density of states $F(\omega)$ comes from a quasi one-dimensional soft mode, that is, one with a strong axial anisotrophy, since in this case $F(\omega) \propto (\omega - \omega_{q_0})^{-1/2}$, q_0 being the location of the soft mode in the Brillouin zone. In $ZrZn_2$ such highly directional soft modes can be qualitatively understood from the fact that the closed-shell configuration is $Zr^{4+}Zn^{2+}Zn^{6-}$ which points to a high degree of ionicity and to strong dielectric renormalization of the phonon frequencies (*8*). It is also in agreement with a narrow *d*-band (*13*) and with a strongly localized spin density (*14*).

A general survey of all *C* 15 compounds of the form ZrM_2 shows immediately why $ZrZn_2$ is such an exceptional case. All metals M, with the exception of Zn, are transition elements, and the resulting compounds are invariably superconducting. The effect of Zn in $ZrZn_2$, which has predominantly *s*− (instead of *d*−) orbitals, is to shield the *d*-electrons of Zr and hence leads to a lattice softening. A confirmation hereof can even be seen directly in its mechanical softness and low melting point. In the elements no such shielding exists so that, because of the stiffness of the *d*-electron binding, the corresponding phonon is a hard mode. This again is reflected by mechanical hardness and high melting temperatures.

The subtlety of our *p*-state pairing hypothesis is readily shown by the following two additional experimental facts. Replacing Zn_2 by CuAl a *C* 15 structure is again obtained. However, the softening of the Zn_2 and therefore the ferromagnetism are lost (*15*). Finally, gradual substitution of Zn by Fe destroys the ferromagnetism at less than 10 atomic percent Fe (*4, 15*) whereas, as is well-known, $ZrFe_2$ which has again the *C* 15 structure is ferromagnetic with a Curie point far above room temperature.

As was stated at the outset, the only other compound known to be an itinerant ferromagnet is Sc_3In. Since similar arguments are likely to apply again, the rarity of this type of compound becomes evident. Will there ever be a third itinerant ferromagnet? Isostructural and isoelectronic with $ZrZn_2$ is only $TiBe_2$. Thus far we only know that it is not superconducting above 1 K.

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Jaundice Phototherapy: Micro Flow-Cell Photometry Reveals Rapid Biliary Response of Gunn Rats to Light

Abstract. *Hepatic pigment clearance in rats can be followed continuously with photometric detectors designed for high-pressure liquid chromatography. This method showed that light has a fast effect on bilirubin metabolism in homozygous Gunn rats, even at low doses and intensities. This is consistent with geometric isomerization of bilirubin IXα as a primary step in phototherapy.*

Phototherapy is an established procedure in neonatal medicine (*1*). It is used prophylactically on babies with neonatal jaundice to prevent bilirubin encephalopathy, which is caused by deposition of bilirubin IXα in the brain. Ephemeral jaundice is common during the early neonatal period because the liver is functionally immature and often unable to clear bilirubin IXα from the circulation in the normal way (that is, by hepatic uptake, glucuronidation, and excretion). In phototherapy, endangered infants with high or rapidly rising plasma levels of bilirubin are irradiated with blue or white lights to diminish circulating bilirubin IXα and reduce the risk of its diffusion into the brain. Usually, irradiation is