CALCULATION OF THE TEMPERATURE DEPENDENCE OF THE KNIGHT SHIFT IN CADMIUM

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The temperature dependence of both the isotropic and anisotropic parts of the Knight shift in cadmium is calculated and found to be in good agreement with experiment. Lattice vibrations effectively decrease the strength of the lattice potential and make it more isotropic. As the temperature increases the energy bands become thus more free-electron-like and the *s* character of the wave functions on portions of the Fermi surface increases. At the same time the cancellation due to different *p* contributions in the various sheets of Fermi surface is destroyed, and the anisotropy also increases.

From the point of view of its nuclear magnetic resonance properties, cadmium is not an ordinary metal. Its unusual properties are the following: (1) The isotropic Knight shift K_{iso} increases[1-4] by about 70% between 4 and 594°K, the melting temperature (see Fig. 1); for an ordinary metal K_{iso} is practically temperature independent, with changes of less then 10%. (2) Upon melting K_{iso} suffers an abrupt increase of 33%; most metals show little change. (3) The anisotropic part of the shift K_{an} also has an anomalous temperature dependence. It starts from a small negative value at 4°K and, after going through zero at a temperature between 4 and 60°K, it increases to a fairly large positive value at the melting temperature (see Fig. 2).

Properties (1) and (3) seem paradoxical, since (1) indicates that the *s* part of the wave functions on the Fermi surface[5] increases with T and (3) seems to indicate that the non-*s* part (and mostly the *p* part) of the same wave functions also increases with T.

We have performed a theoretical calculation of both K_{iso} and K_{an} which agrees well with experiment and resolves the puzzling paradox. Results are exhibited also in Figs. 1 and 2. The calculation has the following characteristics:

(A) It is based on the highly nonlocal pseudopotential determined by Stark and Falicov[6] from Fermi-surface data and proven to work successfully in explaining a variety of experiments.[6-9]

(B) It was carried out at $T = 0$°K, $T = 298$°K, and $T = 462$°K (temperatures at which the lattice parameters are well known[10]) and in the melt.

(C) The electron wave functions were obtained

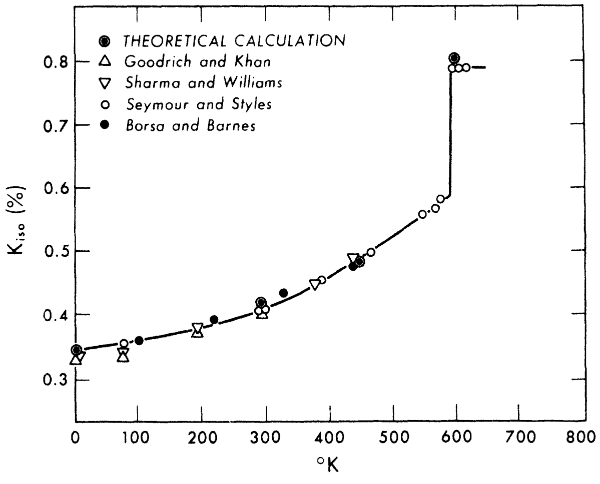

FIG. 1. Experimental data and theoretical calculations for the isotropic part of the Knight shift in ^{113}Cd as a function of temperature.

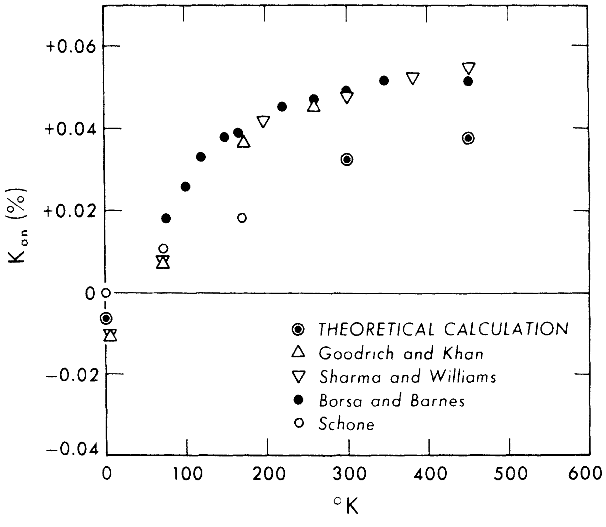

FIG. 2. Experimental data and theoretical calculations for the anisotropic part of the Knight shift in ^{113}Cd as a function of temperature.

from the pseudo wave functions of Ref. 6 by orthogonalizing them to the core states.[11]

(D) The electronic spin susceptibility was calculated at $T \neq 0$, from the standard formula.[5] However, the density of one-electron states corresponds to a new band structure[12,13] in which the structure factor $S_0(\vec{G})$ corresponding to a reciprocal lattice vector $\vec{G}$ is replaced by

$$S(\vec{G}, T) = \exp[-W(\vec{G}, T)]S_0(\vec{G}),$$

where $\exp[-2W(\vec{G}, T)]$ is the usual Debye-Waller factor.

(E) The evaluation of the electron density at the nuclear site involves similar ensemble averages, which introduce additional $\exp(-W)$ factors.[13]

(F) In a similar way the calculation of the dipole-dipole (anisotropic) contribution requires ensemble-averaged wave functions and again the introduction of $\exp(-W)$ factors.[13]

(G) The many-body exchange and correlation effects were taken into account by a constant, temperature-independent enhancement factor in the spin susceptibility; this factor was taken to be 1.55 so as to make the value of K_{iso} at $T = 0$ agree with the experimental value.

(H) In the melt, the pseudopotential was assumed to be exactly zero; the electronic wave functions are thus plane waves properly orthogonalized to the core states and the density of electron states is that of a free electron gas of equal density.

(I) Calculation of all relevant quantities was carried out for a large number of points (~15 000) in the hexagonal Brillouin zone; averages over the Fermi surface were performed by computing values at 43 nonequivalent points on the various sheets of surface.

Results are shown in Table I and Figs. 1 and 2. It is there seen that the agreement with experiment is good. Qualitatively the effect can be explained as follows:

(a) At $T = 0$ the fairly large (and mostly d-like) crystal potential causes a very sizable decrease in the density of states at the Fermi energy from that of a free electron.[8] At higher temperatures the $\exp(-W)$ factors reduce the effective potential and make the density of states become closer to the free-electron value with a resulting increase in the spin susceptibility.

(b) The Fermi surface in the third zone (the so-called lens) is formed by states which have predominantly s-like and p_z-like character about the ion sites; this character is roughly temperature independent.

(c) The first- and second-zone hole surface (the so-called monster) consists mostly of states which in the neighborhood of the ions are mostly s-like and p_x-p_y-like.

(d) The shape and size of the monster are very sensitive to the strength and symmetry of the potential; as T increases the two separate sheets of the monster reconnect to form a single, multiply connected surface similar to those found in zinc and magnesium. Simultaneously additional pieces of electron surface appear in the third and fourth zones around[6,7] the point L.

(e) As T increases and the potential becomes weaker and less anisotropic, the electronic states on the second-zone monster become more s-like and less p_x-p_y-like about the ions.

(f) Therefore, as a result of (a) and (e), the s contribution to the average over the Fermi surface increases with T, with a consequent increase in K_{iso}.

(g) As a consequence of (b), (c), (d), and (e), as T increases the p_x-p_y contribution to the wave-function average decreases, while the p_z part remains essentially unchanged; this causes the small p_x-p_y dominance (negative K_{an}) present at low temperatures to change to a large p_z dominance (positive K_{an}) at higher temperatures.

(h) Upon melting Cd becomes a free-electron-like metal and K_{iso} increases by 33%; this agrees with Ziman's hypothesis[14] and confirms it quanti-

Table I. Values of various relevant quantities.

	Fermi energy (Ry)	Spin susceptibility (cgs volume units)	Relative electron density at nuclear site ···	K_{iso} (%)	K_{an} p part (%)	s and d part (%)	Total (%)
0°K	0.651	0.54×10^{-6}	0.74	0.35	−0.011	+0.005	−0.006
298°K	0.644	0.60×10^{-6}	0.81	0.42	+0.027	+0.007	+0.034
462°K	0.634	0.63×10^{-6}	0.86	0.47	+0.030	+0.007	+0.037
melt	0.547	0.95×10^{-6}	1.00	0.81	0	0	0

tatively.

In summary we would like to point out that the effect as explained by our theoretical calculation arises from the temperature washing out of electronic structural effects present at $T=0$, which are due to strong pseudopotentials.

These structural characteristics do not appear in free-electron-like metals (e.g., Na, Mg, Al), but they are not peculiar to Cd alone. Zinc, which electronically resembles Cd so much in many other respects, should be a good candidate for investigation if the rather difficult experimental conditions it imposes could be overcome.

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LOW-q PHONONS AND THE WIDTHS OF LOW-ENERGY ELECTRON-DIFFRACTION PEAKS

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Low-q phonons cause local distortions of the crystal lattice which cause the gaps in the electronic band structure to wobble up and down. This results in a broadening of the peaks in low-energy electron diffraction which otherwise would be much narrower than observed, according to recent calculations. The effect varies with temperature and energy as $T^{1/2}E^{3/4}$ in rough agreement with experiment.

Recent calculations[1,2] of intensity/energy curves for low-energy electron beams reflected from crystal surfaces contain sharp peaks whose widths vary, but are characteristically between 1 and 2 eV wide. On the other hand, experimentally observed peaks,[3] while corresponding with the theoretical peaks in their mean positions, differ by an order of magnitude in width, being characteristically about 10 eV wide for energies between 100 and 200 eV. This is the paradox for which we wish to offer an explanation. Other phenomena any theory must account for are as follows: Firstly, although the intensity-versus-energy peaks are broadened, the angular broadening of the beams is negligible[4] for well-prepared surfaces. Secondly, the observed peaks become wider at higher energies,[5,6] whereas in a simple theory[7] the widths are equal to the band gaps in the electronic band structure of the solid, which shows finer structure at higher energy.[2] Thirdly, although increasing temperature lowers the intensities of the peaks drastically by approximately the Debye-Waller factor,[5] their widths remain substantially unchanged and are certainly not narrowed by the same factor as the simple picture would suggest.[8] There is one more fact in the situation. Calculations have been performed with the spacing of the first atomic layer slightly larger than in the bulk[9] and with a complex potential to represent inelastic processes[9,10]: Neither