Comments and Addenda

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Comments on Origin of Solvent Knight Shifts in Alloys

R. E. WATSON*
Brookhaven National Laboratory,† Upton, New York 11973
L. H. BENNETT
Institute for Materials Research, National Bureau of Standards, Washington, D. C. 20234
AND
A. J. FREEMAN‡
Physics Department, Northwestern University, Evanston, Illinois 60201
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The various sources of changes in solvent Knight shifts upon alloying, and nonlinear effects are examined.

RECENTLY, Van Ostenburg and Alfred (VOA) have stated[1] that a numerical error led the present authors to an erroneous conclusion concerning the source of solvent Knight shifts in nonmagnetic alloys.[2] We differ with this and the conclusion stands: There exist significant contributions to the Knight shifts in addition to those yielded by standard phase-shift analyses, for Ag-Cd and Cu-Zn (for which we reported numerical results) and for many other systems, including the alloys of polyvalent metals. The discrepancy between their and our plotted theoretical results is associated with the use of specific-heat data γ to estimate the Pauli susceptibilities χ_p appropriate to the Knight shifts. Both the VOA and our results are derivable from the same γ data depending on how one chooses to employ these data. In our view, our choice is based on stronger physical grounds. The basis of a choice is of some physical interest to the alloy problem in general and not just to Ag-Cd and Cu-Zn (the specifics of our choice for these two systems have been described elsewhere).[3] As we indicated previously, specific-heat data are, at best, an uncertain source of information on how χ_p varies with alloying. It can be argued that no physical conclusions should be based on such data and that the one serious error in our previous work was one of judgment for having used the data at all. It was not essential to our conclusion, namely, that there are several contributions of the same order of magnitude to solvent Knight shifts and that a model involving one alone is not physically correct.

We have already shown[2,3] that a model involving some aspects of rigid-band theory predicts solvent Knight-shift changes with as great numerical accuracy as phase-shift estimates based on Friedel charge screening.[4] This would indicate that the latter are not unique in their ability to reproduce experiment and that *neither model alone* produces an adequate description of the Knight-shift behavior. Both screening and Fermi-level shifts should be significant in the more concentrated alloys to which we attached the greatest relevance for our estimates. (The applicability of our model to the very dilute region is not completely obvious, but it appears[5] that changes in the Fermi wave vector albeit reduced are important even in this region. On the other hand, screening has physical significance for any concentration of impurities, although the model has actually been evaluated only for noninteracting, hence infinitely dilute, impurities.) Crudely, the Knight shift here is the product $\chi_p H_{\text{eff}}$, where H_{eff} is some suitably averaged hyperfine field appropriate to Fermi surface conduction electrons. In the illustration given,[2,3] the screening and rigid-band (our P_F) treatments yield

* Also Consultant, National Bureau of Standards.
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[1] D. O. Van Ostenburg and L. C. R. Alfred, Phys. Rev. Letters **20**, 1484 (1968).
[2] R. E. Watson, L. H. Bennett, and A. J. Freeman, Phys. Rev. Letters **20**, 653 (1968); **20**, 1221(E) (1968). There was an error in the theory curves as labeled in the original letter (see Erratum); VOA, among others, uncovered the existence of this error. Correcting for this yields curves with slopes of the *same sign and magnitude* as before, not with the opposite sign plotted by VOA (Ref. 1).
[3] L. H. Bennett, R. W. Mebs, and R. E. Watson, Phys. Rev. **171**, 611 (1968).
[4] J. Friedel, Phil. Mag. **43**, 153 (1952); Nuovo Cimento **2**, 287 (1957).
[5] E. Stern, Phys. Rev. **168**, 730 (1968).

predictions of the same sign and magnitude (to a factor of 2) for the change in H_{eff} on alloying. In addition, we made a crude estimate of the effects of changes in χ_p on our rigid-band predictions. VOA questioned numerical details of this estimate, while claiming unmatched success for screening results,[6] which omit χ_p altogether. Any significant actual change[7] in χ_p upon alloying damages this numerical success. (Most other published screening analyses neither claim nor strive for exact numerical agreement.) It is our opinion that any change in χ_p must also be accounted for when comparing screening theory with experiment. In any case, the two models should be compared on an equal basis (i.e., not one model with, and the other without, consideration of the real changes in χ_p).

Let us consider the more interesting physical question of how the various experimental observables vary with alloy concentration. There is growing evidence that a linear concentration dependence, spanning both the very dilute and more concentrated regions, is the exception. This is of considerable interest, argues the importance of continued careful experimentation, and will lead us to a second point of disagreement with VOA. The scatter in the NMR data of Rowland[8] and others is such that nothing but a straight line, covering a broad concentration range, could reasonably be drawn through it. Deviations from linearity, particularly in the most dilute region, could be seen in a variety of data (previous studies, e.g., the Pb-alloy results of one of us)[9] but in general the deviations lie well within experimental uncertainties. Recently, Anderson *et al.*[10] have reported results for indium alloys. They report a steep initial slope in the isotropic Knight shift followed by a dip (at $\sim 1\%$ concentration of Pb or Sn), in turn followed by a curve with a flatter slope. Not only did their results require care in measurement and data reduction, but, more pertinent here, the details were only picked up by studying a large number of samples which differed only slightly in impurity concentration from one to the next, especially below 2%. The structure they uncovered would probably have been missed with the sort of concentration sampling characteristic of earlier studies on other systems. Arguing, after Anderson, Thatcher, and Hewitt's fact, we believe that there are strong suggestions, at least, of nonlinear structure in earlier results and that this (in addition to the satellites discussed previously[2]) should be the subject of careful experimental study. Nonmonotonic Knight-shift variations cannot be explained in terms of current screening models or in terms of our P_f variation alone.

There are distinct suggestions of nonlinearity with concentration in other experimental observables such as γ. This takes us to the disagreement in estimating the changes in χ_p from γ data. The Cu and Ag alloys of immediate interest here are diamagnetic and it is difficult to obtain any sensible estimate of the change in χ_p from susceptibility measurements. We, therefore, turned to the stated dangerous[2,3] assumption that changes in χ_p are linearly related to changes in γ. The γ data for either system displays a steep initial slope with considerable (and inevitable) scatter in data points, followed by a dropoff in slope at larger concentrations. In view of the fact that electron-phonon and other extraneous effects are likely to be most important in the very dilute range and the fact that the Knight-shift lines are assumed linear for the full range of available data, we obtained least-squares straight-line fits of γ (first[2] by eye and subsequently[3] by computer, these yielding almost identical results) over the 0–24% and 0–29% range for Cu-Zn and Ag-Cd, respectively. The Cu-Zn Knight-shift data do not extend this far out, but the fitted change in γ for 0–10% Zn is almost the same. None of our fitting procedures weight the pure metal γ more heavily than the alloys, since it is relative changes in χ_p which interest us. Our fits lie within the stated error bars of γ. The plotting of ratios of raw data points, as done by VOA is quite inappropriate (we also think their curves weight too heavily the initial slope). In short, we believe they inadequately accounted for the nonlinearity of the γ behavior. Their plotted points become doubly inappropriate when one notes that the experimental (γ) error bars which should be attached to these points are as large as the dimensions of VOA's figures. This discussion is a bit academic since there are increasing grounds for believing that γ and χ_p changes are not proportional to one another on alloying. More specifically, results based on the γ fits should have little effect on the conclusions which should be drawn from our Letter. As previously noted,[2,3] Henry concluded[11] from his susceptibility measurements that χ_p decreases on alloying contrary to the γ behavior but in keeping with current rigid-band predictions[12] for Cu and Ag. Recently Clune and Green have observed[13] that electron-phonon effects contribute an increase in γ on

[6] L. C. R. Alfred and D. O. Van Ostenburg, Phys. Rev. **161**, 569 (1967).

[7] Changes in χ_p are not readily incorporated into screening theory that was derived (Ref. 4) for the infinity dilute impurity region (where χ_p may be considered constant). Most workers are careful either to apply their results to that limit, or to be suitably cautious when comparing with experiment for more concentrated systems. We might further note that the core s terms which were the origin of our rigid-band effect will also quantitatively affect screening predictions.

[8] T. J. Rowland, Phys. Rev. **125**, 459 (1962).

[9] R. J. Snodgrass and L. H. Bennett, Phys. Rev. **132**, 1465 (1963).

[10] W. T. Anderson, Jr., F. C. Thatcher, and R. R. Hewett (private communication); Phys. Rev. **171**, 541 (1968).

[11] W. G. Henry and J. L. Rogers, Can. J. Phys. **38**, 908 (1960).

[12] Brillioun-zone effects cause marked differences from free-electron theory as utilized by VOA (Ref. 1).

[13] L. Clune and B. A. Green, Bull. Am. Phys. Soc. **13**, 643 (1968); (private communication). In the case of Pb-Tl alloys, the electron-phonon contribution to the specific heat, known from superconductivity tunneling experiments, causes γ to increase, whereas, the bare density of states decreases on alloying. A similar sign reversal seems possible for the noble metal alloys, though the conclusion here is less certain.

alloying of such a magnitude that the χ_p for Ag-Cd and Cu-Zn certainly does not rise as fast as the initial increase in γ and might, in fact, be expected to drop (given the observed increases in γ). In other words, χ_p may very well decrease upon alloying. In any case, the detailed behavior of χ_p is irrelevant to our physical conclusions. There appear to be several contributions of the same magnitude to the Knight-shift variation. Fortuitous cancellation of terms may occur for some systems.

We had concentrated[2,3] on noble metal alloys as illustrations, but similar Knight-shift behavior is seen for polyvalent metals such as Al and Pb. The rigid-band description is equally applicable here (yielding[14] crude quantitative agreement), whereas, the particular screening treatment[6] for which VOA claim success and cannot and wasn't meant to describe the experimental results. This does not imply that screening is not occurring here also. Again, we seem to be dealing with several Knight-shift contributions and whatever cancellation (or augmentation) of terms occurs for Cu-Zn or Ag-Cd, it is certainly different here. As said before,[2] a unified model is clearly needed.

[14] We leave this as an exercise for the student, using Fig. 5 of Ref. 3.

Erratum

Thermal Conductivity of Superconducting Tin Films in a Magnetic Field, JOHN E. SMITH, JR., AND D. M. GINSBERG [Phys. Rev. **167**, 345 (1968)]. The following typographical errors should be corrected. The factor $2/\rho$ appears twice in Eq. (2.9) and once in Eq. (2.11). This factor should be replaced by $\frac{1}{2}\rho$ in each of these places. The second minus sign in Eq. (2.9) should be replaced by a multiplication sign. The plus sign in Eq. (5.5) should be replaced by a minus sign. Our calculations were performed with the correct equations.