ly, there is still the possibility that the difference between these estimates and our results is simply due to slow convergence or other peculiarities in the expansion procedure.

Our results, which are expected to simulate for $|\epsilon| \gtrsim 10^{-2}$ an infinite two-dimensional kinetic Ising system[13,14] with nearest-neighbor interactions, lead to the following conclusions:

(1) The divergences of $\tau^{\pm}$ and $\tau_{(nl)}{}^{\pm}$ are predicted to be the same as those of the isothermal susceptibility [Eq. (11)]. Consequently, there is no evidence for a critical speeding up of fluctuations. The equality of Δ and $\Delta_{(nl)}$ confirms the conjecture of Suzuki,[4] and $\Delta_{(nl)} \approx \gamma \approx \frac{7}{4}$ agrees with the result of Ogita *et al.*[12]

(2) The critical exponent Δ_A of slowing down of the order-parameter autocorrelation function is considerably smaller than that of the isothermal susceptibility [Eq. (11)].

(3) Our results [Eq. (11)] do not confirm the estimates obtained from the high-temperature expansion and ratio method.[4,9,11]

(4) Our data [Eq. (11)] imply that

$$\tau^{\pm}/\tau_A{}^{\pm} \sim |\epsilon|^{+x}, \quad x \approx -\tfrac{3}{4}.$$

This result contradicts the prediction of the DSH, $x = -\frac{1}{4}$ [Eq. (9)], and the estimates from the high-temperature expansion and ratio method, which in turn confirm the DSH.

To summarize, we have reported on computer simulations of critical slowing down in finite kinetic Ising systems which approximate an infinite system for $|\epsilon| \gtrsim 10^{-2}$, [13,14] as one expects from static scaling for the rounding effect. The critical exponents deduced from these data disagree with the predictions of the DSH to such an extent that the failure of this hypothesis in the kinetic Ising model is probable. Our results also disagree with those obtained from a high-temperature expansion and ratio method.

We acknowledge fruitful discussions with R. Kubo, P. C. Hohenberg, Y. Imry, and H. Yahata.

[1]R. A. Ferrell, N. Menyhard, H. Schmidt, F. Schwabl, and P. Szepfalusy, Ann. Phys. (New York) 47, 565 (1968), and Phys. Lett. 18, 891 (1967).

[2]B. I. Halperin and P. C. Hohenberg, Phys. Rev. 177, 952 (1969), and Phys. Rev. Lett. 19, 700 (1967).

[3]H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Clarendon Press, Oxford, England, 1971).

[4]M. Suzuki, Int. J. Magn. 1, 123 (1971).

[5]For a discussion of the DSH for the kinietic Ising model we refer to K. Kawasaki, Progr. Theor. Phys. 40, 706 (1968).

[6]M. Suzuki and R. Kubo, J. Phys. Soc. Jap. 24, 51 (1968).

[7]M. Suzuki, H. Ikari, and R. Kubo, J. Phys. Soc. Jap. Suppl. 26, 153 (1969).

[8]M. Suzuki, Progr. Theor. Phys. 42, 1076 (1969).

[9]H. Yahata and M. Suzuki, J. Phys. Soc. Jap. 27, 1421 (1969).

[10]M. Suzuki, Progr. Theor. Phys. 43, 882 (1970).

[11]H. Yahata, J. Phys. Soc. Jap. 30, 657 (1971).

[12]N. Ogita, A. Ueda, T. Matsubara, H. Matsuda, and F. Yonezawa, J. Phys. Soc. Jap. Suppl. 26, 145 (1969).

[13]E. Stoll and T. Schneider, Phys. Rev. A 6, 429 (1972).

[14]E. Stoll, K. Binder, and T. Schneider, Phys. Rev. B (to be published).

[15]R. J. Glauber, J. Math. Phys. (N.Y.) 4, 294 (1963).

Tunneling into a High-T_c Superconductor–Nb_3Sn

L. Y. L. Shen
Bell Laboratories, Murray Hill, New Jersey 07974
(Received 11 August 1972)

Tunnel junctions were fabricated on Nb_3Sn films reacted on Nb substrates. Derivative measurements were made from 0 to 50 meV and above 18 K. From these tunneling results, the phonon spectrum of Nb_3Sn is shown to have a strong low-energy peak at 9 meV, a broad peak centered around 17 meV, and a small peak at 25 meV. Using this shape of the phonon spectrum and taking $\mu^* = 0.11$, a maximum T_c of ~21 K is obtained for this class of superconductors. This result suggests that crystal transformations arising from instabilities do not limit T_c in this case.

The tunneling of electrons through an insulator into a superconductor is a powerful way of studying directly the electron-phonon interaction in the superconductor. The technique has been developed, and described in detail, by McMillan and Rowell.[1] The energy gap and the derivatives of

the tunneling I-V characteristics are analyzed, using an iterative solution of the Eliashberg strong-coupling gap equation,[2] to give the gap parameter, renormalization functions in the normal and superconducting states, phonon spectrum weighted by the electron-phonon coupling parameter $[\alpha^2(\omega) \times F(\omega)]$, electron-phonon coupling constant λ, and Coulomb pseudopotential μ^*.

For all materials studied so far,[3,4] the self-consistency of the parameters indicates that only the electron-phonon and Coulomb interactions are required to explain fully the occurrence of superconductivity. In this Letter results of a tunneling study of Nb_3Sn are presented. Although our junctions made on this material are not yet ideal, they are of sufficient quality to determine the energy gap and shape of the Nb_3Sn phonon spectrum, which clearly shows a peak at a surprisingly low energy. Extrapolation of our results to ideal junction behavior indicates that $\lambda = 1.55$ to 1.69 for Nb_3Sn, and hence, from the dependence of T_c on λ derived by McMillan,[5] the maximum T_c one can expect for materials of the Nb_3Sn family is 20 to 21 K.

Previous tunneling studies of β-tungsten superconductors have generally been confined to measurement of the energy gap, which was generally reduced by impurities on the surface. The junction and surface quality is easily judged in these cases by the magnitude of the tunnel current flowing for $eV \ll \Delta$ at $T \ll T_c$. However, a well-defined tunneling characteristic for Nb_3Sn and energy gap of 2.8 meV ($2\Delta = 3.6kT_c$ if $T_c = 18$ K) were obtained by Levinstein and Kunzler[6] using a point contact, but instability of the point prohibited derivative measurements. Hauser, Bacon, and Haemmerle[7] avoided the surface contamination problem on V_3Si by studying a V_3Si-Al/Al-oxide/Pb proximity sandwich. They reported a gap of 2.8 meV ($2\Delta = 3.8kT_c$ for $T_c = 17$ K), but structures they observed in the derivative curves are difficult to interpret quantitatively in these n-s sandwiches because of interference effects.[8]

The preparation of Nb_3Sn films on Nb was first reported by Jackson and Hooker.[9] Dickey, Strongin, and Kammerer[10] reported the superconducting transition temperature of 14 K in such a Nb_3Sn film. We have used the same method to generate clean Nb_3Sn surfaces in an ultrahigh-vacuum environment. The vacuum was provided by a 60-liter, all metal titanium sublimation pump, 9000 cm^2 in area, capable of reaching an ultimate pressure $\sim 2\times10^{-11}$ Torr. The detailed description of the sublimation pump is to be published elsewhere.[11] Because of the extreme sensitivity of the junction quality to the experimental parameters, the junction must be prepared with extreme care. First, a sheet of Nb of size 7.0 cm × 0.5 cm × 0.12 cm was heated for $\frac{1}{2}$ h near its melting point at 10^{-9} Torr. Second, a thin layer of Sn (300 Å) was evaporated at 10^{-10} Torr over the clean Nb surface at room temperature. Third, the Sn-coated Nb was heated again to 700 C in a vacuum of 10^{-10} Torr. Fourth, the very reactive Nb_3Sn layer was oxidized in air at room temperature and a layer of Pb was evaporated at 10^{-5} Torr over the oxidized Nb_3Sn surface to complete the junctions. The outgassing procedure, amount of Sn, and annealing temperature are all critical to the preparation of good junctions and under the wrong conditions junctions can be prepared showing the Sn gap, Nb gap, and Nb_3Sn gap (in addition to the Pb gap), and various proximity effects. With the proper thickness of the Sn layer and room-temperature air oxidation, the resistance of the Nb_3Sn-O-Pb junction is $\sim 0.1\ \Omega/mm^2$. The superconducting I-V characteristic of such a junction (naturally the best made to date) at 1.5 K is shown as curve 1 in Fig. 1. The first major rise in current occurs at Δ_{Pb} (1.35 meV) and is due to a small amount of normal or gapless metal on the Nb_3Sn surface. No abrupt rise in current is observed at the energy $\Delta_{Pb}+\Delta_{Sn}$ (1.95 meV), indicating that no free tin is present. The second rise in current occurs at $\Delta_{Pb}+\Delta_{Nb}$ (2.85 meV). Then, the current gradually increases and becomes linear with voltage above $\Delta_{Pb}+\Delta_{Nb_3Sn}$ (4.45

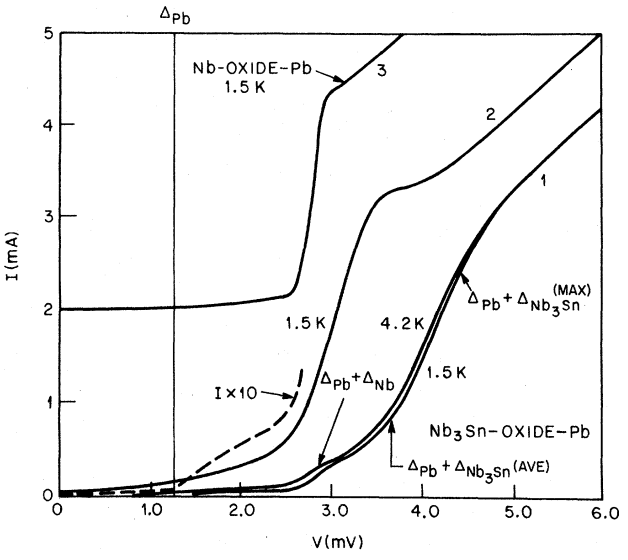

FIG. 1. The I-V characteristics of three Nb-containing junctions.

meV). This complicated behavior is characteristic of a superconductor-superconductor proximity sandwich, i.e., Nb_3Sn film on superconducting Nb substrate. We can see from curve 1 in Fig. 1 that very little change in the I-V characteristics occurs when the junction cools from 4.2 to 1.5 K, the slight increase of the Pb gap at 1.5 K being as expected. To illustrate the problems encountered with other Nb_3Sn surfaces, curve 2 in Fig. 1 is the I-V curve of a Nb_3Sn-O-Pb junction made by evaporating Pb directly onto RCA vapor-deposited Nb_3Sn magnet ribbon which superconducts at 17 K. This junction characteristic indicates the presence of a thick normal-metal layer and the "gap" is barely bigger than that of Nb as shown in Fig. 1, curve 3, for a Nb-O-Pb junction. No phonon-induced structure was found in junctions such as that of curve 2. It is interesting to note that the "knee" structure just above the "gap" in the I-V curves 2 and 3, which has been associated[12] with a contaminated surface (essentially a n-s proximity sandwich), is not present in the best Nb_3Sn junction. From curve 1, the average energy gap of this Nb_3Sn layer is ~2.5 meV, although it is obvious that some areas have Δ as high as 3.1 meV. In another slightly poorer junction, where T_c measurements were also made, these gaps were $\Delta_{av} = 2.0$ mV and $\Delta_{max} = 2.8$ mV, while the first sign of a gap in the tunneling characteristic was seen at 16.4 K and a strong development of a gap observed at 12 K. This gives $\Delta_{av}/12\ \mathrm{K} = 1.94$, and $\Delta_{max}/16.4\ \mathrm{K} = 1.98$, very reasonable values for a strong-coupling superconductor.

In Fig. 2 the measured conductances of the junction of curve 1 of Fig. 1 are shown for the normal and superconducting states and compared to similar measurements for the best Nb-O-Au junction we have ever made. The Nb data were plotted using the top voltage scale and the Nb_3Sn data were plotted using the bottom voltage scale. The relative shift of the two scales by $\Delta_{Nb_3Sn} - \Delta_{Nb}$ facilitates direct comparisons of the energies of the phonon-induced structures of two different materials. Note that the normal-state characteristic of the Nb-O-Au junction was obtained at a field of 8 kG. As we increase the magnetic field on the Nb_3Sn-O-Pb junction the Pb gap disappears at ~5 kG and with it all the phonon-induced structure of the Pb counter electrode. The Nb-induced gap at 1.5 meV disappears below 8 kG, but even below this field there is no evidence of phonon-induced characteristics from the Nb base layer. This suggests that the Nb_3Sn completely covers the Nb and

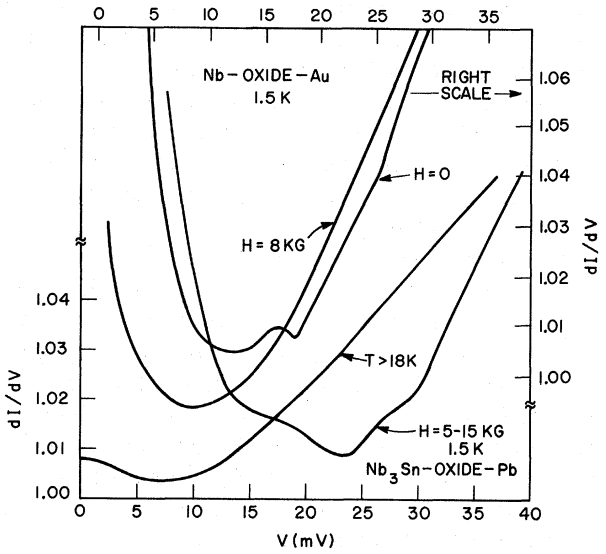

FIG. 2. The curves of dI/dV versus V for Nb and Nb_3Sn. The two upper curves are measured by the top voltage scale, and the two lower curves by the bottom voltage scale.

that the Nb gap is indeed seen in the I-V characteristic by a proximity effect. Above 5 kG and up to our magnet limit of 15 kG, the Nb_3Sn tunneling characteristic is independent of field and, as shown in Fig. 2, clearly reveals phonon-induced drops in quasiparticle density of states from 19 to 22 meV and also near 28 meV (measured from $V = 0$). The normalized first derivative and second derivative (Fig. 3) show these structures more clearly and further indicate the presence of another structure in the Nb_3Sn density of states at 9 meV (measured from Δ_{Nb_3Sn}). No further structure was observed from 30 to 50 mV and noise in the junction prohibited measurements above 50 meV. The phonon density of states of Nb_3Sn, weighted by the electron-phonon coupling parameter $\alpha^2(\omega)$, was calculated using the McMillan program, taking $\Delta_{av}(Nb_3Sn) = 2.3$ meV, and is shown at the bottom of Fig. 3. This value of Δ was chosen to give the best fit between the measured density of states and the BCS density of states from Δ to $\Delta + 5$ meV.

The most surprising features of this spectrum, when compared to that of Ta or Nb, are the low-energy peak at 9 meV and the breadth of the 17-meV peak. From neutron scattering and tunneling experiments it is known that the transvere and longitudinal peaks in the Nb are both sharp, and occur at 16.6 and 23.5 meV.[12] The 9-meV peak in Nb_3Sn is presumably the "soft phonon

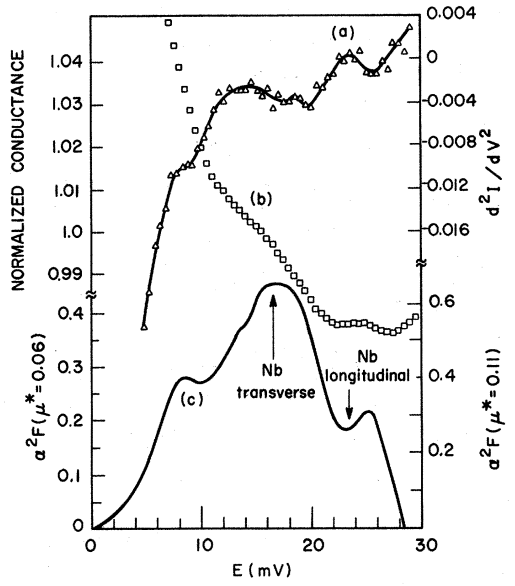

FIG. 3. The top curve is the second derivative d^2I/dV^2 plotted versus $V-\Delta_{Nb_3Sn}$. The middle curve is the normalized first derivative. The bottom curve is α^2F plotted according to the left-hand scale. α^2F should be measured against the right-hand scale if μ^* was fixed at 0.11.

mode" associated with the lattice instabilities discussed by Batterman and Barrett[13] and by Testardi *et al.*[14] The resultant strong weighting of the phonon spectrum towards low energies (compared to Nb, for example) leads to high T_c's, as discussed by McMillan.[5]

The quality of tunnel junctions, and hence validity of the derived coupling parameters, can generally be judged from the value obtained for μ^*. In all tunneling experiments on easily prepared materials μ^* is determined to be 0.10 to 0.15 and theoretical calculations[15] show 0.10 to 0.18 to be a reasonable value. From the data of Fig. 3 we obtain $\mu^*=0.06$ and $\lambda=1.08$ for Nb_3Sn with $\Delta=2.3$ meV. These low values of both μ^* and λ we take as an indication of a slightly contaminated Nb_3Sn surface, as similar reductions in μ^* and λ are observed in Nb and dirty Ta junctions.[12] The normal niobium base layer could also be a factor here, although if the Nb_3Sn layer is more than a few coherence lengths thick (the coherence length being that determined at the phonon energy) the tunneling characteristic should measure Nb_3Sn only.

It is of interest to examine the effect of these new results for Nb_3Sn on the predictions of maximum superconducting transition temperatures made by McMillan.[5] By assuming that the β-tungsten materials have a phonon spectrum with a shape similar to that of niobium, McMillan showed that the strong-coupling theory predicts an absolute limit on T_c when $\lambda>2$. That is, whatever attempts are made to increase λ, by alloying for example, no gain in T_c will be made once λ has reached ~2. McMillan further points out that attempts to increase λ may well first lead to lattice instabilities and resultant crystal transformation. Hence, he essentially suggested two operative limits on the maximum T_c, the "$\lambda=2$ limit" or a lattice transformation at $\lambda<2$. In the case of Pb-like materials the $\lambda=2$ limit gives $T_{c\,max}=9.2$ K and a $Pb_{70}Bi_{30}$ alloy has a T_c of 8.6 K.[16] However, in the V_3Si family McMillan calculates $T_{c\,max}=40$ K,[5] compared to an unobserved 17 K for V_3Si itself, suggesting that the lattice instability limit is important here. In Nb_3Sn materials the prediction is $T_{c\,max}=28$ K, compared to 20.7 observed for Nb_3(Al-Ge)[17] and 20.3 K for Nb_3Ga.[18] However, this estimated $T_{c\,max}$ will be revised if the Nb_3Sn phonon spectrum differs greatly from that of Nb. As Fig. 3 now shows this to be the case, we proceed to recalculate $T_{c\,max}$ for materials with an $\alpha^2(\omega)F(\omega)$ similar in shape to that of Fig. 3(c). To do this, we need to estimate the $\alpha^2(\omega)\times F(\omega)$ result for a perfect tunnel junction. We believe that the gap Δ_0 would be 3.1 meV ($2kT_c$ for $T_c=18$ K), and that μ^* should fall in the range 0.11 to 0.15. We further assume that the shape of $\alpha^2(\omega)F(\omega)$ of Fig. 3(c) would be unchanged, i.e., the relative heights of the peaks are kept fixed and the magnitude of the whole spectrum is increased by a factor independent of energy. This increased magnitude, found by a single solution of the gap equation with $\Delta_0=3.1$ meV and $\mu^*=0.11$, is shown as the same curve in Fig. 3(c), but measured with the new α^2F scale to the right. The spectrum, essentially a measure of the attractive part of the electron-electron interaction, must be increased by 44% and 60% to give self-consistently a gap of 3.1 meV when opposed by a Coulomb repulsion represented by 0.11 and 0.15 pseudopotentials. From these scaled spectra we obtain $\lambda=1.55$ if $\mu^*=0.11$ and $\lambda=1.69$ when $\mu^*=0.15$. From the dependence of $T_c/T_{c\,max}$ on λ calculated by McMillan,[5] this gives $T_c/T_{c\,max}=0.85$ and 0.9, respectively, or $T_{c\,max}=21.2$ or 20.2 K for $\mu^*=0.11$ or $\mu^*=0.15$. This rather startling result appears to indicate that, although instabilities and low-frequency phonon modes are important in the spectrum of Nb_3Sn and hence in determining T_c, the "$\lambda=2$ limit" of the strong-coupling theory is already approached in Nb_3(Al-Ge) and

Nb_3Ga, and the crystal transformations resulting from instabilities are not the important limiting factor on T_c in this family of materials.

The author wishes to thank J. M. Rowell for a critical reading of the manuscript. The author wishes to thank especially W. L. McMillan for his suggestion on how to estimate the maximum T_c.

[1]W. L. McMillan and J. M. Rowell, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969), p. 561.

[2]G. M. Eliashberg, Zh. Eksp. Teor. Fiz. 38, 966 (1960) [Sov. Phys. JETP 11, 696 (1960)].

[3]J. M. Rowell and R. C. Dynes, in *Phonons*, edited by M. A. Nusimovici (Flammarion, Paris, 1971), p. 150.

[4]R. C. Dynes, Solid State Commun. 10, 615 (1972).

[5]W. L. McMillan, Phys. Rev. 167, 331 (1968).

[6]H. J. Levinstein and J. E. Kunzler, Phys. Lett. 20, 581 (1966).

[7]J. J. Hauser, D. D. Bacon, and W. H. Haemmerle, Phys. Rev. 151, 296 (1966).

[8]J. M. Rowell and W. L. McMillan, Phys. Rev. Lett. 16, 453 (1966).

[9]A. G. Jackson and M. P. Hooker, in *Structure and Chemistry of Solid Surfaces*, edited by G. A. Somorjai (Wiley, New York, 1969), p. 73–1.

[10]J. M. Dickey, M. Strongin, and O. F. Kammerer, J. Appl. Phys. 42, 5808 (1971).

[11]L. Y. L. Shen, to be published.

[12]L. Y. L. Shen, in *Superconductivity in d- and f-band Metals*, edited by D. H. Douglass (American Institute of Physics, New York, 1972), p. 31, and references therein. K. Schwidtal, J. Appl. Phys. 43, 202 (1972).

[13]B. W. Batterman and C. S. Barrett, Phys. Rev. Lett. 13, 390 (1964).

[14]L. R. Testardi, T. B. Bateman, W. A. Reed, and V. G. Chirba, Phys. Rev. Lett. 15, 537 (1965); L. R. Testardi, Phys. Rev. B 5, 4342 (1972), and in "Physical Acoustics," edited by W. P. Mason and R. N. Thurston (to be published).

[15]P. Morel and P. W. Anderson, Phys. Rev. 125, 1263 (1962).

[16]J. G. Adler and T. T. Chen, Solid State Commun. 22, 1961 (1971).

[17]G. Arrhenius, E. Corenzwit, R. Fitzgerald, G. W. Hull, H. L. Luo, B. T. Matthias, and W. H. Zachariasen, Proc. Nat. Acad. Sci. U. S. 61, 621 (1968).

[18]G. W. Webb, L. J. Vieland, R. E. Miller, and A. Wicklund, Solid State Commun. 20, 1769 (1971).

Calculation of Electric Field Gradients in Crystals Using Molecular Wave Functions*

D. R. Taylor
Department of Physics, Queen's University, Kingston, Ontario, Canada
(Received 11 July 1972)

The electric field gradient in stressed NaCl is calculated using a simple cluster approach. The assumption of independent bonding allows the contribution of cluster electrons to be calculated directly from their wave functions, without the use of shielding factors. Molecular rather than atomic wave functions are employed. Good agreement with experiment is obtained.

Although electric field gradients at nuclear sites in crystals have been routinely measured for a number of years by a variety of techniques, theoretical studies of the origin of the electric field gradient (EFG) have had only limited success. Most theories of solids assume inert and spherical atomic cores, a fatal approximation since the EFG interaction goes as R^{-3} from the nucleus and, hence, small perturbations of the inner electrons are likely to be important. This point has been recognized in recent years, and it has been shown in detail[1] that an EFG arises from the fact that core orbitals lose their spherical symmetry due to overlap with neighboring ions. The most complete calculation of this kind was done by Sharma[2] for Al_2O_3, using free-ion wave functions and including all the metal-ligand matrix elements. In spite of the good agreement achieved in this case there remain two major difficulties with this approach: (1) The use of free-ion wave functions restricts its validity to the most ionic solids, and (2) there is no consistent way of taking account of shielding and antishielding effects; for example, if ions A and B overlap, the EFG due to the charges on A and B may be calculated with the use of appropriate Sternheimer shielding factors,[3] but to the charge distributed in the "overlap region" no such shielding factor obtains. This is a serious problem since these shielding corrections are typically large.

This Letter proposes a new theoretical ap-