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Influence of impurities on the solute electric field gradient in noncubic s-p metals

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A study of electric field gradients at nontransitional dilute impurities in polyvalent metals is reported. The electric field gradients show a systematic dependence on the valence difference between impurity and host. A charge-screening mechanism of conduction electrons, relating the density of impurity p states to the resulting field gradients, can explain the observed correlation.

Experiments on the quadrupole interaction of excited nuclear states in noncubic metals have yielded a large number of coupling constants in the past few years. Most of these data naturally come from probes present as dilute impurities in metals. The crucial question about the magnitude of the electric field gradient (EFG) measured at the site of the impurity, compared with the pure metal's value, is not yet generally solved despite many efforts in this direction.

To get a systematic access to this problem we have studied a limited set of binary systems, namely, noncubic s-p metals where the conduction electrons stem from the outer atomic s-p shells of the elements and impurities of the same structure. We have used the time-differential measurement of perturbed angular distributions of in-beam recoil-implanted nuclei into Zn, Cd, In, Sn, and Sb.[1] This method proved a powerful tool to obtain systematic data in addition to existing coupling constants mostly from γ-γ angular-correlation measurements. Evaluation of our data for a Ge probe gave a first systematic hint that the EFG's measured depend on both the probe and the host matrix, and we suggested charge-screening effects as a main reason.[2]

An especially attractive probe for enlarging our data set is $^{67}\mathrm{Zn}^m$ because it features the same number of electrons outside closed shells (two) as does the much-studied ^{111}Cd. A comparison of probes with identical number of outer electrons in different matrices can particularly help to elucidate the contribution of conduction electrons to the EFG. The probes ^{67}Ge and ^{204}Pb with four outer electrons form another pair with a rather complete set of data.

In the following analysis of existing coupling constants in the s-p metals we show that an impurity effect on the solute EFG's exists exhibiting regular features and we can demonstrate that charge screening plays a dominant role in this coupling of impurity and host.

An expression which reveals the possible influence of the impurity on the resulting EFG is the ratio of this EFG at an impurity site P in a host H to the EFG of the pure metal ($P=H$),

$$V_{zz}(P,H)/V_{zz}(H,H) \ . \tag{1}$$

The quadrupole moment is known in each case with sufficient accuracy to deduce V_{zz}. We know that the main contribution to V_{zz} for all s-p matrices of our study is due to local conduction electrons (V_{zz}^{el})—an empirical result which could be theoretically confirmed recently.[3-5] It is then evident that the EFG at an impurity site should be very sensitive to changes in the conduction electron wave functions around this site. These changes can be brought out by the electron redistribution around impurities by which the charge difference between impurity and matrix is screened out mainly within a short distance around the impurity atom. A detailed treatment of this effect can be found in Ref. 6.

To see whether this charge screening manifests itself in the EFG we plot the set of ratios of Eq. (1) for the different probes P in each matrix H as a function of the valence difference between impurity and matrix δZ. The valence for all matrices and impurities considered is the number of outer s-p electrons, which is a well defined quantity in these alloys since d electrons, in a first approximation, do not contribute to the conduction band. A slight modification of the numerical value of the valence difference is introduced when the size difference of host atoms and impurity is taken into account. The resulting expansion or contraction of the lattice around the probe changes the effective excess charge to be screened. This can be calculated in the framework of elastic continuum theory; the first consideration of the effect is due to Blatt.[7] For our study on polyvalent metals we use the formula of Farrell *et al.*[8] for the actual screening charge

$$\begin{aligned} &\delta Z = Z - Z_0(1+\beta) \ , \\ &\beta = \tfrac{1}{3}[(1+\nu)/(1-\nu)](\delta V/V_0) \ . \end{aligned} \tag{2}$$

Z, Z_0 are the valences of impurity and matrix, ν is

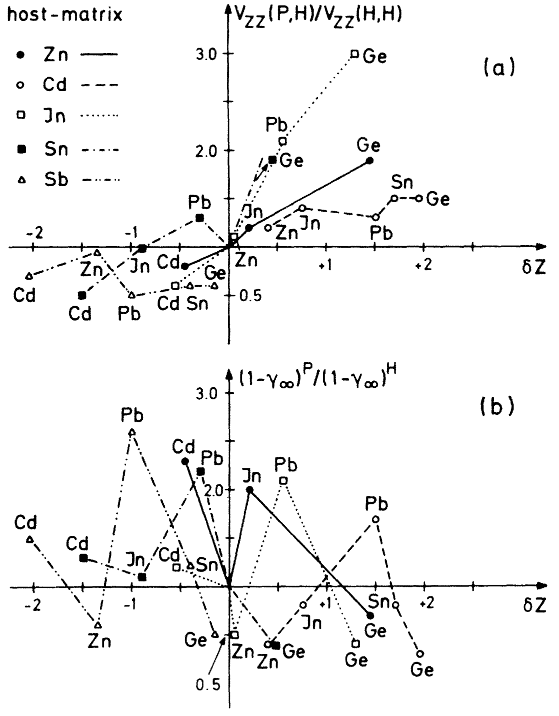

FIG. 1. (a) Ratio of the EFG at probe atoms $[V_{zz}(P,H)]$ in different host matrices to the EFG of the respective pure host $[V_{zz}(H,H)]$ plotted vs the valence difference δZ between probe and host. The data for each host are connected to guide the eye. (b) Ratio of the Sternheimer factor of the probe atom $(1-\gamma_\infty)^P$ to the factor $(1-\gamma_\infty)^H$ of the host plotted in the same manner as in (a) (data from Ref. 14).

Poisson's ratio, and $\delta V = V - V_0$ is the volume difference taken from the pure metal atomic volumes.

The ratios [Eq. (1)] with all analyzed data are displayed in Fig. 1(a), (for a reference of the data see Ref. 9). We note the striking result that all points occur in quadrants I and III. ($\mathrm{Sn}^{204}\mathrm{Pb}$ is no real exception. The solute EFG's in the Sn matrix increase with increasing δZ as do all the other data, a slight miscalibration of the absolute EFG of Sn is possible.) In the case of no impurity effect on the EFG all ratios should be equal to one, the remarkable ordering with increasing δZ indicates that charge screening is a significant process leading to EFG's at the impurity different from the pure metal's value. It should be stressed that remaining uncertainties of the quadrupole moments involved do not destroy the unique trend of Fig. 1(a)—a constant increase of the EFG's with increasing δZ.

Whereas the charge screening mechanism is uncovered empirically with this figure, the theoretical application to the problem of solute EFG's is by no means straightforward. There is no direct way of expressing the EFG changes in terms of impurity scattering as can often be done in other problems dealing with dilute alloys. For pure metals there exists on the one hand a theoretical approach by Mohapatra *et al.*[4] indicating that the whole k space should contribute to the conduction electron part of the EFG but on the other hand Watson *et al.*[10] suggest that for metals with a high density of states at the Fermi surface this part of the k space could be strongly responsible for the EFG. Keeping these difficulties in mind we try to understand the observed behavior of Fig. 1(a) by considering the charge screening of a free electron gas which under the influence of the ionic potential then contributes to the resulting EFG.

The behavior of the charge screening is best described with the derivative of the phase shifts η_l,

$$N_l(k) = (2/\pi)(2l+1)d\eta_l/dk \qquad (3)$$

for the density of impurity l states near the probe nucleus.[6] We are facing two questions: what is the structure of the impurity screening in terms of Eq. (3) and how can this structure be linked to the EFG's on the probe atoms? As a tractable model we use the ideas of Watson *et al.*[10] which predict a linear dependence of V_{zz}^{el} on the density of states of electrons near k_F. For the structure of the screening charge we can simplify Eq. (3) considerably: it was pointed out[6] that mostly p-like electrons are responsible for charge screening in the s-p metal alloys, and p waves on the other hand contribute most significantly to V_{zz}^{el}. So we can concentrate on $l = 1$. Equation (3) with $l = 1$ and $k = k_F$ should therefore directly describe the change of the EFG in a metal due to impurity screening.

Considering the behavior of $d\eta_1/dk$ at k_F we take the calculations of Leonard[11] as a guideline for the behavior of these p wave phase shifts as a function of δZ which were explicitly performed for polyvalent metals. For $0 \le \delta Z \le 2$ positive $d\eta_1/dk$ at k_F are obtained which increase with increasing δZ, and accordingly negative derivatives for $\delta Z < 0$. This leaves us, via Eq. (3), with a picture of increasing solute EFG's with increasing δZ, and the reverse trend for $\delta Z < 0$, since $N_1(k_F)$ gives the amount of electron density due to charge screening. This picture of the overall effect is surprisingly well supported by the experimental data in Fig. 1(a), which gives for the first time a strong indication that a charge screening concept works to explain relevant features of EFG's at impurities. This is all the more surprising in view of the complicated band structure calculations employed to compute the EFG, for example, in Cd.[4]

We point out that if the EFG should depend sensitively on the whole *k* space we would have no formula to predict the influence of charge screening on its magnitude. But as the derivatives $d\eta_1/dk$ are very similar at all values *k* for $|\delta Z| \leq 2$,[11] and therefore also the screening charge, we can at least assume that the influence on the EFG goes in the same direction for all values of *k* even if we cannot use a simple proportionality between the density of the screening charge and the EFG. This difficulty could, on the other hand, lead to an attractive situation: to measure solute EFG's with large δZ to probe the contributing regions of the *k* space. At large positive δZ the derivatives $d\eta_1/dk$ behave so differently for *k* near the band bottom and near the Fermi surface, that their sign can become different. This might prove an experimental tool to obtain further insight into the structure of V_{zz}^{el}.

In a recent work Raghavan *et al.*[12,13] have shown that starting from the customary decomposition of the EFG, $V_{zz} = V_{zz}^{\mathrm{lat}}(1-\gamma_\infty) + V_{zz}^{\mathrm{el}}$, there exists a universal correlation between $V_{zz}^{\mathrm{lat}}(1-\gamma_\infty)$ and V_{zz}^{el}, which can be approximately given as $V_{zz}^{\mathrm{lat}}(1-\gamma_\infty) \propto V_{zz}^{\mathrm{el}}$. Superimposed on this correlated structure are certainly other effects, as can be seen from the rather large scatter of data points especially for the dilute *s*-*p* alloys[13] under consideration in the present paper. The proportionality between $V_{zz}^{\mathrm{lat}}(1-\gamma_\infty)$ and V_{zz}^{el} reduces the expression $V_{zz}(P,H)/V_{zz}(H,H)$ of Fig. 1(a) to $(1-\gamma_\infty)^P/(1-\gamma_\infty)^H$. We plotted this last ratio[14] versus the same δZ axis as in Fig. 1(a), see Fig. 1(b). Apparently, there is no correlated trend in these curves, showing that the charge screening by conduction electrons is indeed an independent and strong additional effect in these dilute *s*-*p* alloys.

As a final remark we mention that the relation between the density of *p* states and the EFG at impurity sites should obviously lead to a conservation of the sign of the pure matrix's EFG's as has been shown to hold by a large number of measurements of Raghavan *et al.*[13]

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