Nuclear magnetic resonance in aluminum alloys. II

Yuh Fukai and Kenji Watanabe
Department of Physics, Chuo University, Kasuga, Bunkyo-ku, Tokyo
(Received 3 December 1973)

The core enhancement factor of Al is recalculated by use of Bloch wave functions, and estimates reported in our previous paper of wipe-out numbers and electric field gradients on the first and the second neighbors of impurity atoms in Al alloys are revised accordingly. The revision is found to make the existing discrepancy between theory and experiment more conspicuous. It is concluded that the scattering of Bloch waves instead of plane waves should result in an appreciable enhancement in magnitude as well as anisotropy of the screening charge distribution, and offer an ultimate solution of the problem.

In our previous paper,[1] hereafter referred to as Paper I, pseudopotential calculations as well as experiments on quadrupole interactions have been reported on a series of Al alloys. A comparison between theory and experiment in terms of wipe-out numbers and the electric field gradient (EFG) on the first and second neighbors of an impurity atom revealed that these quantities were consistently underestimated. The discrepancy was there attributed to the use of oversimplified wave functions. The purpose of this paper is to report an improved estimate of the core-enhancement factor, and thereby help ascertain possible defects of the theory.

The EFG produced by conduction electrons and acting on a nucleus at a distance r from a scattering center is approximately given by[2,3]

$$eq(r) = \tfrac{8}{3}\pi e\alpha\,\delta n(r), \tag{1}$$

where $\delta n(r)$ is a smooth part of the screening charge density without taking account of a rapidly varying part arising from interactions with core electrons. The effect of the latter is approximately factored out as α, the core-enhancement factor, defined by

$$\alpha = \frac{\int d\vec{R}(\psi_{\vec{k}})^2[1+\gamma(R)]R^{-3}P_2(\cos\theta_{\vec{k}\vec{R}})}{\int d\vec{R}(\psi^0_{\vec{k}})^2R^{-3}P_2(\cos\theta_{\vec{k}\vec{R}})}. \tag{2}$$

$\gamma(R)$ is an antishielding function, $\psi_{\vec{k}}$ is a wave function of a conduction electron on a Fermi surface, and $\psi^0_{\vec{k}}$ is the one approximated by a plane wave. The wave function $\psi_{\vec{k}}$ may be written as

$$\psi_{\vec{k}} = \psi^{\mathrm{OPW}}_{\vec{k}} + \frac{1}{N}\sum_{\vec{q}}{}'\sum_{l} e^{-i\vec{q}\cdot\vec{R}_l}\frac{w(\vec{q})}{E_{\vec{k}}-E_{\vec{k}+\vec{q}}}\psi^{\mathrm{OPW}}_{\vec{k}+\vec{q}}, \tag{3}$$

where $w(\vec{q})$ is a pseudopotential, and the sum over $\vec{q}$ excludes $\vec{q}=0$.

In the calculation of EFG in the present paper, only the core-enhancement factor α is recalculated by using Bloch wave functions; the screening charge density used is the one derived in Paper I as a result of free-electron screening of pseudopotentials.

In the first calculation of α for Al by Blandin and Friedel,[3] a single-orthogonalized-plane-wave (SOPW) approximation corresponding to the first term only of Eq. (3) was adopted, and yielded $\alpha(\mathrm{SOPW}) = 10$.[4] Our previous calculations made a further step by retaining in the sum over lattice sites in Eq. (3) a single term that corresponds to the atom under consideration (a single-pseudowave (SPSW) approximation).[1,5] A value obtained was $\alpha(\mathrm{SPSW}) = 21.8$.[5] In the present calculation, the sum over lattice sites is performed, and, accordingly, the full Bloch character is retained. The second term of Eq. (3) is then written as $\sum_{\vec{G}}{}' w(\vec{G})/(E_{\vec{k}}-E_{\vec{k}+\vec{G}})\psi^{\mathrm{OPW}}_{\vec{k}+\vec{G}}$, in which $\vec{G}=0$ is omitted from the sum over reciprocal lattice vectors. The choice of potentials is the same as in Paper I: Ashcroft's form[6] with a dielectric function without exchange correction has been adopted, with a core radius $R_c = 0.61$ Å for Al.[7] It should be noted that owing to the Bloch character of $\psi_{\vec{k}}$, α is dependent on the direction of $\vec{k}$.

Values of α calculated for three principal directions of $\vec{k}$, i.e., $\langle 100\rangle$, $\langle 110\rangle$, and $\langle 111\rangle$, are listed in Table I, together with a weighted mean value in terms of lowest three cubic harmonics, $\bar{\alpha} = \frac{1}{35}(10\alpha_{100} + 16\alpha_{110} + 9\alpha_{111})$. Dependence of α on the direction of $\vec{k}$ is found to be small in this case, in contrast with other cases studied, Cd and In in Pb,[8] and In.[9]

Wipe-out numbers are obtained by simply multiplying previous estimates by $\bar{\alpha}/\alpha(\mathrm{SPSW})$. This is based on the finding by Tompa *et al.*[10] that calculations yield n nearly proportional to α. On the other hand, EFG on the first and the second neighbor sites are obtained by multiplying previous estimates by $\alpha_{110}/\alpha(\mathrm{SPSW})$ and $\alpha_{100}/\alpha(\mathrm{SPSW})$, respectively. The procedure is approximately valid for metals with a nearly spherical Fermi surface, in which the direction of a scattered wave $\vec{k}$ coming on a point $\vec{r}$ from the scattering center should be almost parallel to $\vec{r}$.

Revised estimates of wipe-out numbers and EFG on the first and the second neighbors of impurity atoms are listed in Tables II and III, respectively.

TABLE I. Core enhancement factor α of Al.

Direction of $\vec{k}$			
⟨100⟩	⟨110⟩	⟨111⟩	Average
α_{100}	α_{110}	α_{111}	$\bar{\alpha}$
14.8	15.6	18.2	16.0

Two different values correspond to screening charge calculations based on two different dielectric functions, *A* without and *B* with exchange correction. Experimental values of wipe-out numbers in Table II are reproduced from Paper I. On the other hand, there has been substantial progress in the last few years in the experimental determination of EFG on near neighbors. They include pure quadrupole resonance (PQR) by field-cycling technique[11] and observations of weak quadrupole structures (satellites) in NMR using either single crystals[12] or powder specimens.[13] Table III lists the most recent data by Drain.[13] It should be added, however, that some of the assignments given in Table III are not without controversy, e.g., second neighbors for Ga and Ge.[14]

A serious discrepancy between theory and experiment is immediately clear from Table II and III: The theoretical estimates amount to only about $\frac{1}{2}$ of the wipe-out numbers and $\frac{1}{3}$ of the EFG on the nearest neighbors deduced from experiments. A similar but less pronounced discrepancy was already noted in Paper I, and was attributed to a negligence of Bloch characters in the calculation. The present calculation of α in terms of Bloch waves has made the point more explicit. It remains to examine whether the inclusion of Bloch characters may enhance the screening charge density by a sufficient amount. Discussions in favor of this are presented in the following.

Let us start with discussions on the electrical resistivity due to impurity atoms and its bearing on the present problem. The resistivity is a useful measure of electron-impurity scattering. Our calculation of the resistivity for Al alloys[7] has

TABLE II. Wipe-out number for Al alloys.

Impurity	Experiment[a]	Theory[b] *A*	Theory[b] *B*
Cu	236	108	116
Ag	205	116	125
Mg	122	57	60
Zn	94	47	49
Ga	160	97	105
Si	199	100	111
Ge	•••	124	137

[a]Data given by Fukai and Watanabe (Ref. 1).
[b]Calculated by use of dielectric function *A* without and *B* with exchange correction.

TABLE III. EFG on the first and the second neighbors of impurity atoms in Al (10^{13} esu).

Impurity	Neighbor position	EFG experiment[a]	EFG theory[b] *A*	EFG theory[b] *B*
Cu	1	9.5	−4.5	+0.6
	2	4.3	+1.4	+2.0
Ag	1	10.4	−4.0	+1.4
	2	5.0	+1.6	+2.2
Mg	1	9.5	−3.9	−1.6
	2	3.0	+0.7	+0.9
Zn	1	8.5	−3.1	−0.8
	2	1.5	+0.5	+0.8
Ga	1	10.7	+2.6	+3.2
	2	2.5	−0.1	−0.1
Si	1	13.2	+5.7	+3.9
	2	3.6	−0.4	−0.7
Ge	1	15.3	+6.5	+4.9
	2	2.5	−0.4	−0.7

[a]Data given by Drain (Ref. 13).
[b]Calculated by use of dielectric function *A* without and *B* with exchange correction.

demonstrated that the inclusion of Bloch characters enhances the resistivity by a factor of about 1.5 over free-electron estimates, and brings theoretical values into close agreement with observation. (In passing, the potentials adopted here for the calculation of EFG are those used for the resistivity calculation referred to above.) A similar enhancement of the resistivity due to Bloch characters has also been reported for vacancies in Al.[15,16] We conclude, therefore, that even in metals like Al, which is generally classified as being nearly-free-electron-like, the effect of Bloch characters in electron-impurity scattering is really significant in magnitude. More pronounced effects are noted for Pb (Ref. 7) and Sn (Ref. 17) alloys, in which the resistivity has been enhanced by factors of 2 and 4, respectively. Observed anisotropy of the impurity resistivity in Sn alloys, characteristic of the tetragonal structure of the matrix, has also been fairly well reproduced in terms of Bloch waves.[17]

In the light of these findings, the following comments on a "standard" method of interpreting EFG in terms of phase shifts will be in order. Since the pioneering work of Kohn and Vosko[2] and Blandin and Friedel,[3] it has become customary to calculate the screening charge distribution in the distant region from phase shifts of plane waves so determined as to reproduce observed resistivity values under the restriction of the Friedel sum rule. Blandin and Friedel[3] noted in particular that the screening

charge density thus derived could explain observed wipe-out numbers for Mg and Zn in Al, if $\alpha = 15$ was assumed. Since this value of α is very close to our present estimate, we find that this sort of phase-shift calculation, in spite of its free-electron character, can lead to the screening charge distribution of the right magnitude. We emphasize that this apparent consistency should be a consequence of the fitting procedure involved. The procedure, in effect, replaces the enhancement of the scattering due to the Bloch character of wave functions by some stronger potential in the free-electron scattering scheme.

More serious difficulties exist in interpreting the observed deviation from axial symmetry of EFG on the nearest-neighbors of impurity atoms. The asymmetry parameter η, which is as large as 0.3 for Ag in Al,[13] could never be explained in terms of free-electron theories because the latter necessarily lead to spherically symmetric charge distribution and, hence, axially symmetric EFG. Examination of trends in Al alloys led Drain to conclude that neither atomic displacements nor local charge imbalance could be a major source of the asymmetry.[13] This asymmetry, we believe, is another manifestation of the Bloch wave scattering. It is instructive to recall in this context that much larger deviations from axial symmetry of EFG on the nearest-neighbor sites have been reported for a number of Cu alloys.[18] As is well known, a Fermi surface of Cu is more strongly distorted than that of Al.

On the theoretical side, the scattering of Bloch waves is rigorously formulated in terms of T matrices, Green's functions, or generalized phase shifts. To the authors' knowledge, however, the only attempt at numerically calculating the screening charge distribution based on Bloch waves is the one by Seeger and Mann for an impurity in Cu.[19] Although ambiguities in a scattering potential detract somewhat from the reliability of their calculation, the resulting anisotropy and the extent of screening charge distribution in certain directions demonstrated beyond doubt the importance of Bloch characters in the screening problem.

In summary, the present calculation as well as recent experimental results on EFG vindicates our previous statement that the effect of Bloch characters is significant in electron-impurity scattering in Al alloys.

---

[1]Yuh Fukai and K. Watanabe, Phys. Rev. B 2, 2353 (1970).
[2]W. Kohn and S. H. Vosko, Phys. Rev. 119, 912 (1960).
[3]A. Blandin and J. Friedel, J. Phys. Radium 21, 689 (1960).
[4]Corrected for an error of a factor of 2 in Ref. 3.
[5]Yuh Fukai, Phys. Lett. A 34, 425 (1971).
[6]N. W. Ashcroft, Phys. Lett. 23, 48 (1966).
[7]Yuh Fukai, Phys. Rev. 186, 697 (1969).
[8]Yuh Fukai, Solid State Commun. 9, 1117 (1971).
[9]Yuh Fukai, J. Phys. (Paris) 33, C3-235 (1972).
[10]K. Tompa, G. Gruner, A. Janossy, and F. Toth, Solid State Commun. 7, 697 (1969).
[11]M. Minier, Phys. Rev. 182, 437 (1969).
[12]L. Jorgensen, R. Nevald, and D. Ll. Williams, J. Phys. F 1, 972 (1971).
[13]L. E. Drain, Proc. Phys. Soc. Lond. 88, 111 (1966); Phys. Rev. 8, 3628 (1973).
[14]Cl. Berthier and M. Minier, Solid State Commun. 10, 257 (1972).
[15]Yuh Fukai, Philos. Mag. 20, 1277 (1969).
[16]R. Benedek and A. Baratoff, J. Phys. Chem. Solids 32, 1015 (1971).
[17]Yuh Fukai (unpublished).
[18]B. L. Jensen, R. Nevald, and D. Ll. Williams, J. Phys. F 2, 169 (1972).
[19]A. Seeger and E. Mann, *Calculation of the Properties of Vacancies and Interstitials* (Natl. Bur. Std. Washington, D.C., 1967), p. 75.