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Nuclear Magnetic Resonance in Dilute Alloys of Mn, Fe, and Cu in Aluminum*

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We have studied the nuclear magnetic resonance of Al^{27} nuclei in very dilute alloys of Mn($\leq$0.049 at.%), Fe($\leq$0.045 at.%), and Cu($\leq$0.30 at.%) in Al. The room-temperature results show line intensities that decrease rapidly with increasing impurity concentration. This decrease is attributed to a wipe-out from the resonance of the Al^{27} nuclei in the vicinity of the impurity, as a result of the interaction of the Al^{27} quadrupole moment with the local oscillating electric-field gradients. The experimental results indicate a wipe-out for the Al:Mn and Al:Fe alloys that is considerably larger than that for the corresponding Al:Cu alloys. This large electrostatic interaction in the case of the transition-metal impurities with unfilled *d* shells is in agreement with the Friedel-Anderson model for such alloys, which describes the screening in terms of resonant scattering of the host-metal conduction electrons by virtual *d* states localized at the impurity site. Using this model, one predicts an increase in the oscillating field gradient on going from Al:Cu to Al:Mn in agreement with experiment. Linewidth measurements in the liquid-helium temperature range show no temperature or magnetic-field dependence, indicating there is no local moment on the impurities.

INTRODUCTION

THE electronic structure of transition-metal impurities in simple metals has been the subject of considerable study in recent years. As a result of the pioneering work of Friedel[1] and his collaborators, a well-defined scheme has developed for treating the problem of impurity states in metals. The impurity, because of its different valency, acts as a scattering potential to the conduction electrons of the metal such that the various outgoing waves in the usual partial-wave expansion of scattering theory are phase-shifted relative to the incoming wave. These phase shifts cause a build-up (or depletion) of electronic charge around the impurity and thereby screen out the excess nuclear charge leaving the system locally charge neutral. This self-consistent screening is expressed mathematically by the Friedel sum rule[2] which relates the screening charge to the various phase shifts of the outgoing partial waves:

$$Z=(1/\pi)\sum_{l,\sigma}(2l+1)\delta_l^{\sigma}(E_F)\,, \tag{1}$$

where Z is the screening charge, and $\delta_l^{\sigma}(E_F)$ is the phase shift for the lth partial wave evaluated at the Fermi energy, and σ denotes the spin. If the impurity is nonmagnetic the spin-up and spin-down phase shifts are identical. In addition to locally screening the impurity charge, the phase-shifted outgoing partial waves give rise to a long-range oscillating charge density in the metal of the form[3]

$$\rho(r)=A\cos(2k_Fr+\eta)/r^3\,, \tag{2}$$

where k_F is the Fermi wave vector, and A and η are constants determined by the scattering center. These long-range charge oscillations arise fundamentally from the sharpness of the Fermi surface and have been investigated for nontransition impurities by Bloembergen and Rowland,[5] and more thoroughly Rowland[6] and Webb[7] who used the interaction of the nuclear quadrupole moments of the host-metal nuclei with the electric-field gradients which accompany such charge oscillations as a probe for studying these effects. The experimental results are in generally good agreement with theory as shown by Kohn and Vosko,[3] and Blandin and Friedel.[4]

The situation in the case of transition-atom impurities (e.g., the 3*d* series) is somewhat less clear and has not been studied experimentally. Qualitatively in terms of the above ideas, one expects the $l=2$ phase shift to dominate the screening and the associated charge oscillations because of the unfilled *d* shell of the impurity atom. To see in detail why this is the case, it is useful to consider the problem from a different point of view. Anderson[8] has developed a theory for such transition metal impurities based on the effect of *s*-*d* mixing on the localized states of the transition atom. The essential feature of the Anderson theory is the formation via this *s*-*d* mixing of virtual bound *d* states within the host-metal conduction band. When a conduction electron is incident on the impurity with an energy near that of the virtual bound state it undergoes resonant scattering and the corresponding phase shift for the resonant partial wave is large. Since for the transition atom impurity the virtual states in question are *d* states, the $l=2$ phase shift arises from resonant scattering and dominates,[9] all other phase

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† Alfred P. Sloan Foundation Fellow.

[1] J. Friedel, Can. J. Phys. **34**, 1190 (1956); Nuovo Cimento Suppl. **7**, 287 (1958); *Metallic Solid Solutions* (W. A. Benjamin, Inc., New York, 1963), Chap. XIX.

[2] C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963), p. 341.

[3] W. Kohn and S. H. Vosko, Phys. Rev. **119**, 912 (1960).

[4] A. Blandin and J. Friedel, J. Phys. Radium **21**, 689 (1960).

[5] N. Bloembergen and T. J. Rowland, Acta Met. **1**, 731 (1953).

[6] T. J. Rowland, Acta Met. **3**, 74 (1955).

[7] T. J. Rowland, Phys. Rev. **119**, 900 (1960); M. B. Webb, J. Phys. Chem. Solids **20**, 127 (1961).

[8] P. W. Anderson, Phys. Rev. **124**, 41 (1961).

[9] A. P. Klein and A. J. Heeger, Phys. Rev. **144**, 458 (1966).

shifts being small. These arguments, together with the Friedel sum rule immediately lead to the following simple expression for the $l=2$ phase shift in the case of interest here[10]; namely, when the transition impurity has no localized magnetic moment

$$\delta_2(E_F)=\pi N/10, \tag{3}$$

where N is the number of electrons in the unfilled d shell of the impurity, or equivalently the total number of electrons localized near the transition atom impurity in the metal. N is determined by the requirement of charge neutrality[9] as expressed by the Friedel sum rule and thus increases uniformly as one goes across the $3d$ series from Ti to Ni.

Having described the screening in terms of resonance scattering for the transition atom impurity the argument goes as before. Again one expects long-range charge-density oscillations, the amplitude and phase of which will be determined predominantly by the large $l=2$ phase shifts.

In this paper, we present a study of the nuclear magnetic resonance (NMR) of Al^{27} in dilute alloys of the metals Cu, Fe, and Mn in pure Al. Aluminum was chosen as the host metal in order to avoid complications associated with the presence of a localized magnetic moment on the impurity atoms. The experimental results show a strong decrease of the Al^{27} line intensity with increasing impurity concentration. This decrease in intensity arises from the interaction of the Al^{27} nuclear quadrupole moments with the local electric-field gradients and gives information on the amplitude of the charge-density oscillations in the vicinity of the transition atom impurities. The results are found to be fully consistent with the treatment of the transition atom d states in terms of resonant scattering as described qualitatively above. In addition, measurements at low temperatures show linewidths which are independent of temperature and magnetic field confirming that there is no magnetic moment on the Mn or Fe impurities.

THE ELECTRIC-FIELD GRADIENTS AND WIPE-OUT

In a crystalline electric field of cubic symmetry the Al^{27} nucleus ($I=\frac{5}{2}$), subject to an external magnetic field, has $(2I+1)$ energy levels which are split by the Zeeman interaction into an equally spaced multiplet with successive levels separated by $\Delta E=g_N\mu_N H_0$, where g_N and μ_N are the nuclear g value and magnetic moment, respectively, and H_0 is the external field. The relative intensities of the allowed transitions ($\Delta m_I=1$) are in the ratio 5:8:9:8:5 so that 9/35 of the total absorption will come from the "central" transition ($m_I=-\frac{1}{2}\to\frac{1}{2}$) and 26/35 of the absorption will come from the "satellite" transitions ($m_I=\frac{5}{2}\to\frac{3}{2}$, $\frac{3}{2}\to\frac{1}{2}$, $-\frac{1}{2}\to\frac{3}{2}$, $-\frac{3}{2}\to-\frac{5}{2}$). The addition of small amounts of impurity will destroy the cubic symmetry in the vicinity of the impurity thereby introducing locally nonzero electric field gradients. These field gradients interact with the Al^{27} quadrupole moment and remove the degeneracy of the various allowed transitions. When the applied field is large the quadrupolar interaction may be treated by perturbation theory. In first-order perturbation there will be a shift in the frequencies of the satellite transitions but not the central transition. The central transition is shifted in second order.

Assuming axial symmetry for the electric field gradient seen by a given aluminum nucleus in the vicinity of an impurity, the shift in frequency[11] in first-order perturbation is given by

$$\nu_m-\nu_0=\frac{3e^2Qq(2m_I-1)(3\cos^2\theta-1)}{8I(2I-1)}, \tag{4}$$

and in second order

$$\nu_{1/2}-\nu_0=\frac{9(e^2Qq)^2(2I+3)(1-\cos^2\theta)(1-9\cos^2\theta)}{256h\nu_0 I^2(2I+1)}, \tag{5}$$

where ν_0 is the resonant frequency of the unperturbed nucleus, m_I is the magnetic quantum number, θ is the angle between the magnetic field and the radius vector from the impurity to the aluminum atom in question, Q is the nuclear quadrupole moment, and q is the electric-field gradient at the aluminum site. The field gradient is clearly largest at sites near the impurity falling off to zero far away. Near the impurity the quadrupolar frequency shifts may be so large that the various transitions are completely removed from the unperturbed nuclear resonance line (i.e., $\Delta\nu$ is considerably greater than a linewidth). This "wipeout" persists out to sufficiently large distances from the impurity that the field gradient is reduced to a point where the quadrupolar splittings are within a linewidth of the host resonance line. In the *all-or-nothing* model[5] one assumes a critical value for the electric-field gradient q_0 such that if $|q|>|q_0|$ the transition is completely removed from the host line whereas if $|q|<|q_0|$ it contributes fully. The critical-field gradient for the satellite transitions will clearly be much smaller than that for the central transition. In this fashion one defines wipeout numbers for the satellite lines and the central line, ω_s and ω_c, respectively, where ω_s and ω_c are the number of host sites in the vicinity of the impurity at which the electric-field gradient exceeds the appropriate critical value. If c denotes the atomic fraction of solute, and one assumes unit intensity for pure aluminum, the total intensity $I(c)$ from all transitions will be given by

$$I(c)=(26/35)(1-c)^{\omega_s}+(9/35)(1-c)^{\omega_c}, \tag{6}$$

so that one expects a reduction in NMR intensity with increasing impurity concentrations. Although the *all-or-nothing* view is clearly an approximation since there is

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[10] J. L. Deplante and A. Blandin, J. Phys. Chem. Solids **26**, 381 (1965).

[11] M. H. Cohen and F. Reif, *Solid State Physics* (Academic Press Inc., New York, 1957), Vol. 5, p. 321.

undoubtedly a transitional region in the crystal, the model is justified experimentally by the fact that one observes a simple reduction in intensity without appreciable line broadening when impurities are added to the host metal.

The electric-field gradient at the solvent atom sites is believed to result in the most part from a redistribution of conduction electron charge at these sites due to conduction electron scattering at the impurity centers as described qualitatively in the introduction. Assuming a free-electron gas and a spherical-scattering potential $V(r)$ a self-consistent calculation of the charge density distribution around an impurity gives for the asymptotic form at large r[3,4]

$$\rho(r)=(\alpha/2\pi^2)[\cos(2k_Fr+\varphi)/r^3], \tag{7}$$

α and φ are given by

$$\alpha\cos\varphi=\tfrac{1}{2}\sum(-1)^l(2l+1)\sin 2\delta_l(E_F), \tag{8a}$$

$$\alpha\sin\varphi=\sum(-1)^l(2l+1)\sin^2\delta_l(E_F). \tag{8b}$$

Here $(2l+1)$ is the degeneracy associated with the lth partial wave and $\delta_l(E_F)$ is the corresponding phase shift evaluated at the Fermi surface. The above expression, having been derived from a standard phase-shift analysis is presumably valid whether or not there is an unfilled d shell. However, in the particular case of resonant scattering the equivalence between the Anderson model and the Friedel phase-shift theory has been demonstrated.[9] One therefore expects an expression of precisely the above form to follow directly from the Anderson model. This is in fact true as is shown in Appendix A. Having obtained the charge-density oscillations, the resulting electric-field gradient takes the form

$$q=(2\alpha/\pi r^3)\cos(2k_Fr+\varphi). \tag{9}$$

The above expression for the field gradient must be modified to be applicable to the case of a real metal where the electronic wave functions are Bloch waves rather than simple plane waves. Furthermore, the actual field gradient at a nucleus must be corrected for antishielding by the core. These effects have been discussed by Kohn and Vosko,[3] and Blandin and Friedel[4] with the conclusion that the field gradient in a real metal is given by

$$q=(2\alpha/\pi r^3)\mu\cos(2k_Fr+\varphi), \tag{10}$$

where μ is an enhancement factor arising from the effects described, and α and φ are as given in Eqs. (8a), (8b), and (9). It is to be noted that the enhancement factor μ is a property of the host metal so that within a given host system relative comparisons can be made independently of μ. An orthogonalized plane-wave calculation by Blandin and Friedel gives $\mu\sim5$ for aluminum. This value appears to be too small to account for Rowland's data on the quadrupolar wipeout in dilute Al:Mg and Al:Zn alloys. Blandin and Friedel suggest a value of $\mu\sim15$ in order to explain the experimental results. In what follows, we shall assume $\mu=15$; although the final conclusion regarding the relative effects of the various solute atoms are independent of this choice.

The calculation of the field gradient therefore relies on the knowledge of the phase shifts. When nontransition atoms are dissolved into the host lattice the conduction electron scattering is "normal" in the sense that the resulting wave function is calculated assuming simple potential scattering. One then has $\delta_0>\delta_1>\delta_2\cdots$ and generally a knowledge of only the first two phase shifts is needed to obtain an adequate estimate of α and φ. For impurity atoms with partially filled $3d$ shells the Friedel-Anderson model predicts resonant scattering for $l=2$ with a large phase shift as given by Eq. (3) above. Assuming the full fivefold orbital degeneracy for a transition atom impurity, an inspection of Eqs. (3), (8a), (8b), and (9) suggests an appreciably larger electric-field gradient at solvent atom sites from resonant scattering than would be expected from simple potential scattering. A relative measure of these effects can be obtained from the wipeout data described in the following section.

EXPERIMENTAL PROCEDURES AND RESULTS

All measurements were made using a high-level oscillator of the type described by Knight[12] with the rf level set at about 1 V. The external magnetic field was obtained from a PEM 12-inch magnet with a 3-in. gap and a field inhomogeneity over the sample volume ($\sim$1 cm^3) of less than 0.5 Oe. The magnetic field was modulated at 43 cps with a modulation amplitude of 2-G peak-to-peak. The first derivative of the absorption signal was recorded after conventional audio amplification and phase-sensitive detection. In all cases the oscillator was held at a fixed frequency and the magnetic field was slowly swept through resonance. Time constants of a few seconds were adequate to obtain signal-to-noise ratios of the order of 50 or better. The oscillator coil was wound and glued onto a cylindrical Plexiglas form. The sample geometry was concentric with that of the form and for each alloy care was taken to ensure that the sample position in the coil was identical for each measurement. The sample volumes were purposely made approximately equal and final corrections and normalization were made by weighing each of the samples. To assure that the samples were unaffected by rf field gradients at the ends of the coil form, their center positions were always close to the geometric center of the coil, and the sample volume was significantly less than that of the coil form.

Since absolute intensity measurements were required for the various alloys studied, a reference-standard signal was necessary. The proton signal from the Plexiglas coil form was a convenient reference and all measurements were made relative to this standard signal. The reference signal had a linewidth of about 5 G and an

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[12] W. D. Knight, Rev. Sci. Instr. 32, 95 (1961).

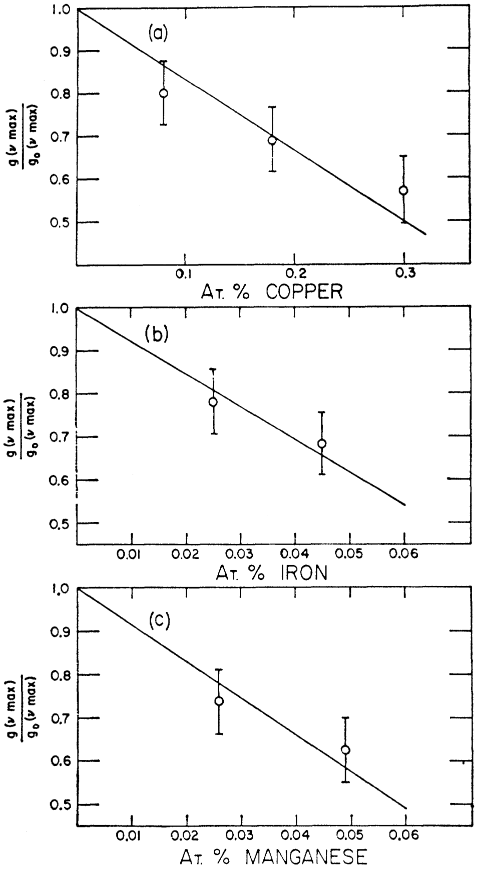

FIG. 1. Peak-to-peak intensity of the Al^{27} absorption derivative as a function of solute concentration for the impurities Cu, Fe, and Mn. The intensity is normalized to unity for no impurity content. The reduction in intensity results from a wipe-out of both satellite and central transition lines.

intensity comparable to that of the Al^{27} signal. The oscillator level was adjusted for each alloy and each measurement to give approximately the same intensity for the proton resonance thereby minimizing errors from changes in Q with the different metal samples. For each alloy studied and each solute concentration the Al^{27} absorption derivative and the proton reference line were alternately recorded leaving the oscillator level and frequency unchanged. Both line intensities were reproducible to within about 2% on successive sweeps provided the sample and coil configuration were left unchanged. If the sample was completely removed from the probe and then replaced the intensity of the Al^{27} line relative to the reference was found to vary by as much as 10%. For each alloy concentration a minimum of five such independent measurements was carried out. The final relative intensity is therefore estimated to have an accuracy of about ±10%.

In all cases the peak-to-peak amplitude of the absorption derivative was taken as a measure of the intensity. This implicitly assumes that the linewidth and line shape is the same for all samples. The experimental results show this to be the case. The measured linewidth for all samples studied was 8.3 G. The line shape was symmetric and the derivative curve between the two peaks was approximately linear indicating that the center portion of the absorption line has the shape of an inverted parabola as is characteristic of the Al^{27} signal.[13]

Three alloy systems were studied, Al:Mn, Al:Fe, and Al:Cu. The alloys were prepared by the Aluminum Company of Canada[14] from superpure base aluminum. Spectrographic analysis of the final samples showed total impurities other than the intended transition elements to be less than 0.01 at.%. Because of the low solubility of transition elements in Al,[15] the alloys studied were restricted to very small impurity concentrations. For the Al:Mn system, Mn concentrations of 0.026 and 0.049 at.% were studied. Similarly measurements were made on alloys with concentrations of 0.025 and 0.045 at.% Fe; and 0.08, 0.18, and 0.30 at.% Cu. These concentrations are well within the known solubility limits as evidenced by lattice constant measurement[16] and other metallurgical studies.

The alloys were filed and the filings were passed through a 325-mesh sieve to ensure that the particles were sufficiently small to avoid absorption-dispersion admixture through particle size effects. The particles were finally magnetically cleaned by passing through a strong inhomogeneous magnetic field.

Room-temperature measurements of the Al^{27} line intensity as a function of solute concentration were undertaken on the above described alloys of Al:Mn, Al:Fe, and Al:Cu in a magnetic field of 7600 Oe. The results are displayed in Fig. 1. It is clear that even for the very low impurity concentrations in question there are significant losses in the host metal NMR intensity. Note that the Mn and Fe impurities cause considerably greater reductions in the Al^{27} line intensity than does Cu. Following the ideas of Bloembergen and Rowland,[5] we interpret the slope of the lines in Fig. 1 as a measurement of the number of Al^{27} nuclei in the vicinity of an impurity that are removed or wiped-out from the main resonance line. Although a single wipeout number is clearly an approximation here since we are dealing simultaneously with first-order (satellite lines) and second-order (central transition) quadrupolar effects, it is a well-defined number which summarizes the data of Fig. 1. With this in mind, the respective experimental wipeout numbers for Al-Cu, Al-Fe, and Al-Mn are 167, 770, and 850, respectively.

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[13] A. G. Redfield, Phys. Rev. 98, 1787 (1955).

[14] We are indebted to Dr. F. T. Hedgcock of McGill University, Montreal, Canada for supplying the Al:Mn samples. For detailed spectrographic analysis, see F. T. Hedgcock, W. B. Muir, and E. Wallingford, Can. J. Phys. 38, 376 (1960). Note, however, for the higher Mn-content alloy, our own analysis gives 0.099 wt.%Mn to be compared with their nominal value of 0.092 wt.%. The Al:Fe and Al:Cu samples were supplied to us by H. E. Schwenger of Aluminum Ltd. Sales, Inc. to whom we are similarly indebted.

[15] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958).

[16] W. B. Pearson, *Handbook of Lattice Spacings and Structures of Metals* (Pergamon Press, Inc., New York, 1958), p. 327.

TABLE I. Scattering characteristics of the aluminum-base alloys.

Solute	Z_{eff}	δ_0	δ_1	δ_2	α	ϕ
Cu	−1.27	−2.03	0.01	···	0.89	1.15
Fe	7	···	···	2.20	4.05	2.20
Mn	6	···	···	1.90	4.76	1.90

The effect of dislocations on the Al^{27} intensity may be estimated from the earlier work of Rowland[6] on Al:Mg. Rowland found that unannealed samples containing 0.64% Mg showed line intensities reduced by ~50% as compared with the same samples after annealing. This effect apparently results from dislocation pinning by the impurities since pure Al is known to self-anneal at room temperature. Consequently, the dislocation wipeout should be proportional to the impurity concentration. For the Al:Mn and Al:Fe samples studied here the maximum impurity concentration is more than an order of magnitude smaller than the 0.64% Mg mentioned above. Consequently, the estimated dislocation wipeout is less than 5% and well within experimental error. For the Al:Cu alloys the concentration is sufficiently high to make dislocation wipeout significant. Thus the wipeout due to quadrupolar effects associated with charge-density oscillations from the copper impurities may be even smaller than the measured value of 167, and it should be considered as an upper limit.

In addition to the room-temperature measurements described above, linewidth and line-shape studies were made at 77, 4.2, and 1.6°K in magnetic fields ranging from 5000 to 10 000 G. Within the limits of experimental error the linewidth, line shape, and Knight shift were found to be independent of the impurity concentrations, temperature and magnetic field. This is in agreement with other measurements[1] on Al alloys indicating that no localized magnetic moment exists on the transition atom impurity in aluminum metal.

ANALYSIS

We first consider the effects of small amounts of copper in aluminum. Copper has a 3*d* shell which is stable, full and below the Fermi level of aluminum. This is simply a restatement of the Friedel sum rule which guarantees local charge neutrality and requires that the number of electrons localized in the 3*d* virtual levels be approximately equal to the number on the free atom. An electron, therefore, incident on the solute atom cannot occupy a 3*d* state and so the problem reduces to one of simple potential scattering. Thus one needs only to know the first two phase shifts δ_0 and δ_1. These quantities can be estimated from a knowledge of the total screening charge below the Fermi level and the electrical residual resistivity due to the impurity scattering. If the lattice remained unstrained by the presence of impurities the screening charge of the conduction electrons would simply be equal to the valence difference between solvent and impurity. However, the strain parameter $a^{-1}(da/dc)$ for Al:Cu is appreciable so that the effective screening charge Z_{eff} will be given by $Z-(\Delta V/\Omega)$, where $\Delta V/\Omega$ is the fractional change in size of the cell. This effect has been considered by Blatt,[17] who obtains

$$\frac{\Delta V}{\Omega}=Z_A\frac{(1+P)}{(1-P)}\frac{1}{a}\frac{da}{dc}, \tag{11}$$

where P is Poisson's ratio, Z_A is the valence of the matrix and (da/dc) is the change in lattice parameter per fractional atomic solute concentration.

Using a potential which satisfies the Friedel sum rule and a free-electron model, the electrical resistivity of the conduction electrons is given by

$$\Delta\rho=\frac{4\pi c\hbar}{Z_A k_F e^2}\sum_l l\sin^2[\delta_{l-1}(E_F)-\delta_l(E_F)]. \tag{12}$$

Taking $\Delta_\rho=1.0\ \mu\Omega$ cm per at.%,[18] $a^{-1}(da/dc)=0.12$,[16] $P=0.34$, $Z_A=3$ and the free-electron value for the Fermi momentum k_F we then compute the first two phase shifts from Eqs. (1), (11), and (12). These are listed in Table I along with the values of α and ϕ computed from Eqs. (8).

Small amounts of iron or manganese in aluminum have partially filled 3*d* states arising from virtual *d* levels overlapping the Fermi level of aluminum. Conduction electrons incident on these impurities will therefore undergo resonant scattering and the $l=2$ phase shift dominates. The appropriate parameters are again listed in Table I. For the screening charge on the Mn and Fe impurities, we assume 6 and 7, respectively. This is consistent with the Friedel sum rule[1,9] and is in agreement with residual resistivity data for these alloys which show a peak at Cr with successively smaller values at Mn and Fe.[1] The resistivity is expected to be maximum when the nonmagnetic virtual *d* state is half-filled.[1] Consequently, $Z\simeq 5$ for Cr and increases monotonically on going toward the right in the 3*d* transition series. We neglect the nonresonant phase shifts for the Mn and Fe impurities since they can be shown to be relatively small.[9]

In Table II we list the electric field gradient contributions from the charge oscillations at the first 20 neighbors for Al-Cu, the first 50 neighbors for Al-Fe and Al-Mn. Aluminum has a face-centered cubic structure so that the distance between an impurity and a given shell will be equal to $[(n_1^2+n_2^2+n_3^2)^{1/2}]$, where (n_1,n_2,n_3) are the coordinates of a nucleus in that shell (in units of $a/2$) relative to the impurity as origin and crystallographic axes along the cube edges. The coordinates in the positive octant are also listed along with the total number of nuclei in each shell as calculated by consideration of all possible permutations of n_1, n_2, and n_3 consistent with the fcc lattice.

In correlating the electric-field-gradient data with the

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[17] F. J. Blatt, Phys. Rev. **108**, 285 (1957).

[18] D. Turnbull, H. S. Rosenbaum, and H. N. Treaftis, Acta Met. **8**, 277 (1960). ($1\Omega=2.5\times10^{-4}\ e^{-2}\hbar$.)

TABLE II. Contribution to electric-field gradient from charge oscillations in units of 10^{21} cm^{-3} at different lattice sites relative to solute atom.

Shell	1	2	3	4	5	6	7	8	9	10
Coordinates	(011)	(002)	(112)	(022)	(013)	(222)	(123)	(004)	(033) (114)	(024)
No. of atoms in shell	12	6	24	12	24	8	48	6	36	24
Solute Cu	62	−119	66	−31	−0.5	21	−16	−5.7	13	1.9
Fe	1557	−464	244	−201	128	−3.6	−81	46	41	−41
Mn	1551	−645	345	−243	117	35	−104	32	62	−34
Shell	11	12	13	14	15	16	17	18	19	20
Coordinates	(233)	(244)	(015) (134)	(125)	(044)	(035) (334)	(006) (244)	(116) (235)	(026)	(145)
No. of atoms in shell	24	24	72	48	12	72	30	72	24	48
Solute Cu	−9.8	−2.4	7.0	−3.9	−5.3	0.2	4.5	3.0	−1.6	−3.8
Fe	−30	28	29	−28	−3.8	21	16	−6.1	−18	−9.6
Mn	−45	21	39	−33	−13	20	23	−0.2	−20	−16
Shell	21	22	23	24	25	26	27	28	29	30
Coordinates	(226)	(136)	(444)	(017) (055) (345)	(046)	(127) (255) (336)	(246)	(037)	(156) (237)	(008)
No. of atoms in shell	24	48	8	84	24	96	48	24	96	6
Solute Fe	7.5	15	7.6	−5.7	−12	−7.9	2.5	9.7	1.4	−6.2
Mn	3.5	17	13	−2.3	−13	−12	−1.0	9.5	4.9	−4.6
Shell	31	32	33	34	35	36	37	38	39	40
Coordinates	(118) (147) (455)	(028) (446)	(356)	(066) (228)	(057) (138) (347)	(266)	(257)	(048)	(019) (338)	(248)
No. of atoms in shell	96	48	48	48	120	24	48	24	48	48
Solute Fe	−8.7	−5.1	1.6	6.6	7.0	3.1	−2.3	−6.0	−5.9	−2.5
Mn	−10	−8.0	−1.0	6.1	8.7	5.7	−0.4	−5.8	−7.4	−4.8
Shell	41	42	43	44	45	46	47	48	49	50
Coordinates	(129) (167) (556)	(466)	(039) (158) (457)	(239) (367)	(448)	(077) (149) (358)	(00*10*) (068)	(11*10*) (277)	(02*10*) (268)	(059) (349)
No. of atoms in shell	120	24	120	48	24	60	30	48	72	72
Solute Fe	2.0	5.1	5.3	−0.9	−3.9	−4.8	−3.4	−0.4	2.5	4.1
Mn	0.3	4.8	6.5	0.7	−3.4	−5.5	−4.9	−2.1	1.6	4.2

experimentally observed wipeout number one needs to know the critical electric-field gradients q_s and q_c so that only nuclei with $|q| < |q_s|$ make a total satellite contribution to the observed signal and nuclei with $|q| < |q_c|$ a total central contribution. We find that our experimental results may best be interpreted by taking $|q_s| = 6.3\times 10^{21}$ cm^{-3}. As is evident from Table II this is by no means a well-defined cutoff since nuclei in various shells have field gradients so close to the critical value that it is difficult to satisfactorily categorize them in terms of the all-or-nothing model. However, it is consistent with Rowland's suggested value[7] of 6×10^{21} cm^{-3}. The satellite transition wipeout is then computed by summing the total number of nuclei for which $|q_s| > 6.3\times 10^{21}$ cm^{-3}, these values being listed in Table III. Using our estimated value of $|q_s|$, from Eqs. (5) and (6) we compute $|q_c|$ to be 123×10^{21} cm^{-3} from which we calculate the central transition wipeouts. For the small concentrations used in this study Eq. (6) reduces to

$$I(c) = 1 - c[(26/35)\omega_s + (9/35)\omega_c]$$

so that the total wipeout ω_t is related to ω_s and ω_c through the relation

$$\omega_t = (26/35)\omega_s + (9/35)\omega_t.$$

Considering the approximations and assumptions involved and the limits of experimental error, the agreement between the experimental and calculated wipeouts for Al:Cu, Al:Fe, and Al:Mn is excellent. The relative values for Cu, Fe, and Mn increase in the expected manner and even the absolute values are remarkably good. In particular the large difference between Cu when the *d* shell is filled and Mn and Fe where it is only partially filled is clearly evident.

TABLE III. Wipe-out data of the different impurities in aluminum.

	Calculated ($\mu = 15$)			Experimental
Solute	ω_s	ω_c	ω_t	ω_t
Cu	242	0	180	≤ 167
Fe	1022	78	778	770
Mn	1186	54	894	850

Figure 2 displays the asymptotic value of electric-field gradient as a function of $k_F r$ for the specific case of Al:Mn. We see that even as far out as the 43rd neighbors the electric-field gradient is large enough to render the

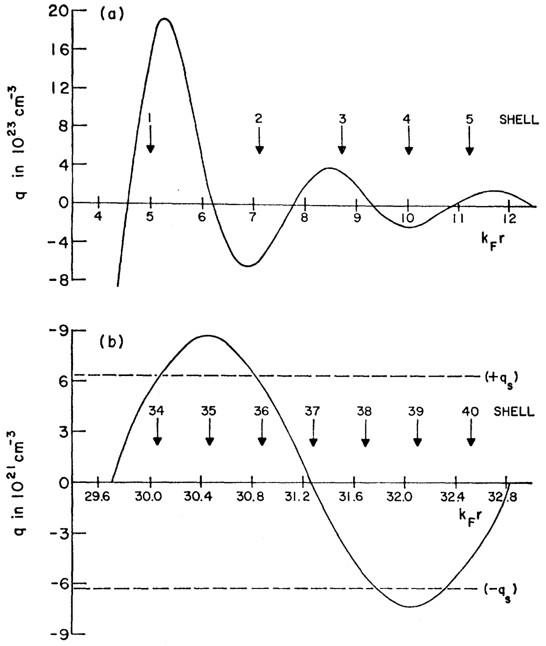

FIG. 2. Asymptotic solution of Hartree-Fock calculation for electric-field gradient distribution around Mn in Al^{27} as a function of $k_F r$. A free-electron gas approximation is assumed with $\mu=15$, $\alpha=4.76$, and $\phi=1.90$. (a) denotes the position of the first five neighbor shells and (b) the positions of more distant shells with electric-field gradients close to the critical value $|q_s|$.

satellite transition components unobservable, i.e., $|q|>|q_s|$. Because we have used powdered materials the frequency shift and hence the field shift will assume all values corresponding to angular factors between +2 and −1 for the satellite components and +1 and −16/9 for the central component. For nearest-neighbor nuclei to transition-metal atoms the expected broadening would be of the order of 1 or 2 kOe, whereas the unperturbed linewidth is 8.3 Oe. This is consistent with the assumption of an all-or-nothing model.

CONCLUSION

The techniques of Bloembergen and Rowland for studying the long-range charge oscillations around impurities in metals have been extended to the case of transition atom impurities. The results are in excellent agreement with theory and give added confirmation of the Friedel-Anderson picture for the electronic structure of transition atom impurities in metals.

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APPENDIX

Kim and Nagaoka[19] have used Green's-function techniques to evaluate the admixture contribution to the spin polarization in the vicinity of a magnetic impurity which is described by the Anderson model. Their calculation may be used directly to evaluate the charge density of interest in this paper. From Eq. (4.12b) of their paper, one obtains

$$\rho(r)=10V^2\int_{-\infty}^{E_F}dE\left\{-\frac{1}{\pi}\mathrm{Im}\left[F_r^2(E)\left(\frac{1}{E-E_d+i\gamma}\right)\right]\right\},\tag{A1}$$

where E_d and γ are the position and width of the virtual levels and the factor of 10 arises from the fivefold orbital and twofold spin degeneracy of the nonmagnetic transition atom impurity. For a free-electron approximation

$$F_r(E)=\frac{v}{4\pi}\frac{2m}{r}e^{i(2mE)^{\frac{1}{2}}r}.\tag{A2}$$

The above integral is evaluated by Kim and Nagaoka, and from their Eq. (B5) one obtains

$$\rho(r)=\frac{5}{\pi^3}\frac{v^2}{E_F}k_F{}^6\left[\frac{E_F-E_d}{(E_F-E_d)^2+\gamma^2}g(2k_Fr)\right.$$
$$\left.+\frac{\gamma}{(E_F-E_d)^2+\gamma^2}\bar{g}(2k_Fr)\right],\tag{A3}$$

where

$$g(x)=(1/x^4)(x\cos x-\sin x),$$
$$\bar{g}(x)=(1/x^4)(x\sin x-\cos x).$$

For $k_Fr\gg1$ the above reduces to

$$\rho(r)=\frac{5}{8\pi^3}\frac{V^2k_F{}^3}{E_F\gamma}\sin\left(\frac{\pi N}{10}\right)\frac{\cos[2k_Fr+(\pi N/10)]}{r^3},\tag{A4}$$

where N is the total number of occupied states on the impurity. Substituting for $\gamma=\pi V^2\rho(E_F)$, where $\rho(E_F)$ is the host-metal density of states (one sign of spin only), and noting that in the free-electron approximation

$$E_F\rho(E_F)=(1/4\pi^2)k_F{}^3,$$

one obtains

$$\rho(r)=\frac{5\sin(\pi N/10)}{2\pi^2}\frac{\cos[2k_Fr+(\pi N/10)]}{r^3}.\tag{A5}$$

Inspection of Eqs. (7) and (8) of the text leads to exactly the same result when only $l=2$ phase shifts are included.

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[19] D. J. Kim and Y. Nagaoka, Progr. Theoret. Phys. (Kyoto) **30**, 743 (1963).