Fe is next to Fe atoms. In using a stainless steel source ( $\gamma$ -phase) the line should shift toward zero velocity in the precipitation process.

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## Valence and Size Contributions to Electric Field Gradients in Dilute Alloys of Silver\*

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A series of measurements has been carried out on alloys of silver to study the electric field gradients produced near solute sites by conduction electron rearrangement (valence effect) and lattice distortion (size effect). The field gradients were measured by observing the attenuation of the angular correlation of cascade gamma rays emitted by Cd<sup>111</sup> nuclei in the alloys. The conclusions of the work are that both valence and size effects are important in determining the field gradients, that the valence effect is longer range than Thomas-Fermi screening predicts, and that the results are best explained by assuming that the lattice distortion is not spherically symmetric.

The attenuation of the angular correlation of gamma rays from In<sup>111</sup> nuclei imbedded in silver has been used to measure electric field gradients around point defects in silver. The technique and some first results are described in a recent paper by Giffels, Hinman, and Vosko.<sup>11</sup> The field gradients around solute atoms are regarded as the consequences of redistribution of conduction electrons as well as the result of more direct field gradient terms arising from the displacement of silver ions in the strain fields around the solute sites. The resulting field gradients at the In<sup>111</sup> sites have the form<sup>2),3)</sup>

$$q = \frac{8\pi\alpha}{3r^{3}}A\cos(2kr + \phi) - \frac{6\beta}{\gamma_{B}}a^{-1}\frac{da}{dc}\frac{1}{r^{3}}$$

where

$$q = \frac{1}{e} \left( \frac{\partial^2 V}{\partial z^2} - \frac{1}{3} \Delta^2 V \right)$$

is the axially symmetric field gradient measured at the  $In^{111}$  site with respect to a coordinate system whose z axis runs from the solute atom through the  $In^{111}$  site.

- r=the distance from the solute atom to the In<sup>111</sup> atom.
- A=amplitude of the charge oscillations assuming the conduction electrons are

represented by plane waves.

- $\phi$ =phase factor in the scattering of conduction electrons by the solute atoms.
- k=wave number of the conduction electrons at the Fermi surface.
- $\alpha$ =a factor taking into account the Bloch modulation of the free electrons and the Sternheimer effect.
- $a^{-1}\frac{da}{dc}$  = fractional change in lattice parameter per unit increase in solute concentration.

 $\gamma_{\scriptscriptstyle B} {=} {3(1 - \sigma) \over 1 + \sigma}$  ;  $\sigma {=}$  Poisson's ratio for silver.

 $\beta$ =an antiscreening parameter of the Sternheimer type.

The field gradient couples with the quadrupole moment of the first excited state of  $Cd^{111}$ , the decay product of  $In^{111}$ , to attenuate the correlation between two gamma rays which use this state as an intermediate one in the cascade.

In this study the quantities  $\alpha$  and  $\beta$  are regarded as adjustable parameters used to fit the data. Using a quadrupole moment of  $10^{-24}$  cm<sup>2</sup> for the Cd<sup>111</sup> nucleus in its first excited state, the figures in Table II show a comparison between experiment and theory of the values of  $\hat{G}_2$ , the average value of the

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solute	Ζ'	$\frac{\Delta  ho}{\mu \Omega}  \mathrm{cm}/\mathrm{At.}\%$	$n_0$	$n_1$	A	$\phi$	$rac{1}{a} rac{da^{\mathrm{b}}}{dc}$
Au	0	0.36	207 .207	.069 069	.0207 .0207	068 .068	00819
Cu	0	0.077	094.094	.031 0.031	.0095 .0095	031.031	0871
Cd	1	0.382	0.521	0.350	0.0276	0.194	.043
Zn	1	0.64	0.521	0.350	0.0276	0.194	0417
Al	2	1.95	2.63	0.171	0.048	-0.164	031
In	2	1.78	2.656	0.162	0.0456	-0.156	.067
T1	2	2.27	2.580	0.187	0.0514	-0.17	.1295
Ge	3	5.5	2.860	0.618	0.0974	0.504	.0071
Pb	3	4.65	2.96	0.584	0.091	0.514	.187
Sn	3	4.36	2.997	0.572	0.0879	0.517	.093
As	4	8.5	3.28	1.000	0.123	1.04	.0347
Sb	4	7.25	3.441	0.947	0.1118	1.028	.146

Table I. Quantities describing the size of the perturbed electronic charge densities and the lattice distortions for the solutes studied.

a) Residual resistivity values taken from A. N. Gerritsen: Handbuch der Physik XIX (1956) 206.

 b) Distortion parameter for germanium is taken from W. Hume-Rothery, G. F. Lewin, and P. W. Reynolds: Proc. Roy. Soc. (London) A 157 (1936) 167; for other solutes, from E. A. Owen and V. W. Rowlands: J. Inst. Metals 66 (1940) 361.

Table II. Comparison of calculations of  $\widehat{G}_2$  with experimental values.

solute	At.%	$\widehat{G}_{2,\mathrm{exp}^{\mathfrak{a}}}$	$\begin{array}{c} \widehat{G}_2\\ \alpha = 45\\ \beta = -40 \end{array}$	$\substack{\widehat{G}_2\\a=0\\\beta=-40}$	$\substack{\widehat{G}_2\\ \alpha=45\\ \beta=0}$	$ \begin{array}{c} \widehat{G}_2 \\ \alpha = 45 \\ \beta = +40 \end{array} $	$\begin{array}{c} \widehat{G}_2 \\ q =  q_v  +  q_s  \\ \alpha = 40  \beta = -37 \end{array}$
Au	.25	$.899 \pm .017$	.945	.991	.941	.942	.938
Au	.42	$.839 \pm .010$	.908	.985	.908	.906	.902
Au	.75	$.685 \pm .017$	.846	.972	.841	.843	.834
Au	1.06	$.696 \pm .040$	.802	.964	.792	.792	.780
Cu	.46	$.785 \pm .012$	.805	.798	.950	.790	.786
Cu	.63	$.742 \pm .017$	.748	.742	.934	.728	.729
Cu	1.28	$.552 \pm .012$	.565	.558	.880	.558	.552
Cd	.50	$.830 \pm .030$	.835	.877	.859	.926	.790
Zn	.50	$.863 \pm .010$	.929	.880	.859	.836	.791
Al	.20	$.904 \pm .030$	.924	.960	.915	.903	.896
In	.45	$.713 \pm .015$	.774	.818	.816	.868	.735
T1	.51	$.655 \pm .010$	.699	.704	.801	.753	.606
Ge	.25	$.843 \pm .016$	.817	.994	.811	.810	.820
Ge	.49	$.688 \pm .019$	.677	.986	.671	.668	.683
Ge	.62	$.620 \pm .013$	.622	.984	.615	.614	.624
Sn	.52	$.627 \pm .022$	.718	.771	.683	.663	.609
Pb	.45	$.708 \pm .013$	.655	.635	.705	.760	.517
As	.62	$.509 \pm .010$	.661	.870	.568	.540	.530
Sb	.25	$.696 \pm .020$	.808	.815	.793	.811	.708
Sb	.51	$.534 \pm .030$	.674	.680	.640	.677	.514
Sb	1.00	$.283 \pm .014$	.510	.490	.436	.509	.293

a) Experimental values of G<sub>2</sub> for Cd, In, Ge, Sn and .51 atomic % Sb are taken from C. A. Giffels, G. W. Hinman, and S. H. Vosko: Phys. Rev. **121** (1961) 1063. Plus-minus values indicate standard deviation for counting statistics.

attenuation factor in the angular correlation. This averaging process is performed over the resolution time of the coincidence circuit and all possible interaction strengths. Table I shows the values of A and  $\phi$  for the various solutes. These are obtained by the method of Kohn and Vosko using the Friedel sum rule and residual resistivities of the alloys.

The agreement between the experimental and the calculated values is on the whole reasonably good. It is clear that both the valence and the size contributions are important. For example the valence effect is dominant for Ge solute while the attenuation in the Cu case comes principally from the size effect. Furthermore, empirically it is found that taking the absolute value of the valence contribution improves the agreement especially in the case of In, Sn, and Sb. Sagalyn, Paskin, and Harrison,<sup>3)</sup> who also observed this effect, attribute it to deviations between the actual strain field and the spherically symmetric one used in these studies as an approximation.

In conclusion we are able to explain the observed field gradients around solute atoms in silver using size and valence contributions of comparable magnitudes. It is necessary for the valence effect to use the long range  $1/r^3$  interaction rather than Thomas-Fermi screening.

A more complete account of these experiments will be published elsewhere.

## References

- C. A. Giffels, G. W. Hinman, and S. H. Vosko: Phys. Rev. **121** (1961) 1063.
- 2 W. Kohn and S. H. Vosko: Phys. Rev. 119 (1960) 912.
- 3 P.L. Sagalyn, A. Paskin, and R.J. Harrison: Phys. Rev. **124** (1961) 428.

## DISCUSSION

Blandin, A. P.: I would like to make two comments:

1) The valence effect is theoretically given mainly by the A and  $\phi$  coefficients. The exact value of  $\phi$  coefficient has not a great importance in NMR experiments, although it may have a much greater importance in  $\gamma$ -correlation experiments. The numerical comparison with experiment is then more difficult in that case, as the semi-empirical value of  $\phi$  calculated by Kohn and Vesko may be dubious.

2) I am surprised by the importance of the strain. This seems to be in contradiction with the results obtained in NMR experiments by Rowland.

**Hinman, G. W.**: I agree that the NMR experiments are probably somewhat less sensitive to the value of  $\phi$  than are the angular correlation experiments. On the other hand  $\hat{G}$  does saturate near 2, so that the angular correlation results are not as sensitive to  $\phi$ , and the deviations from the asymptotic value of q as the results of an experiment that measures q more directly.

The strong attenuation factor with Cu solute is difficult to explain with a small size effect. The calculated values, using  $|q_v| + |q_s|$ , agree better in a number of other cases as well with the size effect included. However, the Pb result is not well explained nor is the Au. We intend to make more exact calculations of the combined size and valence effects in the future.