Temperature dependence of the electric field gradient generated by nearest-neighbor impurity atoms in cubic Ag metal*

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(Received 19 July 1977)

The electric quadrupole interactions produced by near-neighbor (nn) and distant-neighbor impurity atoms of Cu, Au, Zn, In, Ga, Al, Sn, and Sb in a cubic Ag lattice are measured as a function of the temperature by the time differential perturbed angular correlation method. The results show that both the high-frequency interaction ν_Q^h—generated by nn impurities—and the low-frequency interaction ν_Q^l— generated by distant impurities—follow the relation $\nu_Q(T) = \nu_Q(0)\,(1-\alpha T^{3/2})$. From the present measurements it can be concluded that both coefficients, α_h and α_l are strongly dependent on the mass M of the impurity. For the case of Al, Ga, and In impurities with the same charge difference $\Delta Z = 2$ between host and impurity, both α_h and α_l scale as M^{-n} with $n = 0.37 \pm 0.04$ and $n = 0.9 \pm 0.4$, respectively. It is shown that for a Sn impurity the unnormalized slope $\alpha_h \cdot \nu_Q^h(0)$ is independent of the concentration in the range 1.5–3 at.%. A strong dependence of α_h and α_l on ΔZ, the charge difference between host and impurity, is also observed; however, the results do not follow a simple relation.

I. INTRODUCTION

During the recent years considerable interest was focused on the temperature dependence of the electric field gradients (EFG) at nuclear sites in noncubic metals.[1] Experiments using different techniques, such as nuclear magnetic resonance and time-differential perturbed angular correlation (TDPAC), have been performed in order to determine the temperature behavior of the quadrupole frequency $\nu_Q = e^2qQ/h$. As a consequence of these studies[1] it was determined that ν_Q is strongly dependent on the temperature, following the relation

$$\nu_Q(T) = \nu_Q(0)(1 - \alpha T^{3/2}), \tag{1}$$

where $\nu_Q(0)$ is the value of the nuclear quadrupole frequency at $T = 0$ °K and α is a constant.

This result prompted several theoretical works.[2,3] Jena,[2] considering the interaction of the conduction electrons with the phonons of the lattice, and neglecting anharmonic effects, deduced a $T^{3/2}$ expression for the EFG, valid only in a restricted range of temperatures. He also made a prediction about the α dependence on the atomic mass of the host metal which is in contradiction with recent experimental results[4] and calculations.[5] On the other hand, Nishiyama *et al.*,[3] following a similar approach but including anharmonic effects (lattice expansion) by using the available empirical data, obtained good agreement with the experimental results.

We have recently measured[6] the temperature dependence of ν_Q generated by nearest-neighbor (nn) impurities alloyed into cubic Ag host and a similar $T^{3/2}$ law was established. These results showed a strong dependence of the α coefficient on the charge difference ΔZ between host and impurity, and also probably on the mass M of the impurity. At the present stage it is important to perform a systematic study on the temperature dependence of the EFG created by impurities in cubic systems, since it could give information about the basic mechanism involved in this case.

The present work reports the results of temperature dependence of TDPAC measurements in a cubic Ag matrix doped with different impurities. We investigated the temperature behavior of the EFG's created by nn and distant impurities, to the probe nuclear site. Different parameters were changed, like the valence difference ΔZ, the impurity mass M, and also the concentration. As a consequence of these systematics, relevant information was gained, in particular about the mass and concentration influence on the temperature dependence of the EFG.

II. EXPERIMENTAL PROCEDURE AND DATA TREATMENT

The TDPAC experiments were performed through the 173–247-keV γ sequence in the ^{111}Cd nucleus, measuring the interaction of the quadrupole moment of the 247-keV state having lifetime $\tau = 123$ ns with the EFG's produced by the impurities.

The samples were prepared in the following way: First a foil of pure-Ag metal was bombarded with 28-MeV α particles, producing ^{111}In by the ^{109}Ag $(\alpha, 2n)^{111}$In reaction. The radioactive ^{111}In with $T_{1/2} = 67$ h decays to ^{111}Cd which is our probe nucleus. In a second step the impurity was added to the α-irradiated Ag metal, by melting the constituents (purity ≥99.99) in quartz tubes an annealing at 800 °C during some hours, always in argon atmosphere. This means that the samples contain three components: the Ag host, the solute impurity

atoms, and the very dilute radioactive probe atoms of ^{111}In.

The series of Ag-based solid solutions investigated in this paper were all of substitutional type covering a valence difference ΔZ, between Ag and the impurity, form $\Delta Z = 0$ for Au and Cu to $\Delta Z = 4$ for Sb, and also covering a wide range of different impurity mass, from $M = 27$ for Al to $M = 197$ for Au. In the case of Sn impurity, the concentration was also changed. For each impurity the electric quadrupole interaction was measured as a function of temperature in the range from 77 to about 700 °K. At temperatures below room temperature a cold finger was used and for temperatures above room temperature measurements were made in a standard resistance heater with a temperature controller giving a stability of ±2 °C.

The automated angular correlation apparatus was basically a conventional fast-slow coincidence with two NaI(Tl) detectors and a time-to-pulse height converter coupled to a 1024-channel analyzer. The time resolution of the electronic system was 3 ns which permitted frequency measurements up to ~1000 MHz. Due to the fact that we were also interested in observing small amplitude effects of the nn contributions to the EFG, it was essential to perform all the experiments with high statistics; in most of our data the number of coincidences per channel at $t = 0$ was at least 5×10^5.

For the case of perturbation by electric quadrupole interactions in random polycrystalline sources the TDPAC function has the form

$$W(\theta,t) = \sum_k A_{kk} G_{kk}(t) P_k(\cos\theta) , \tag{2}$$

where the differential attenuation coefficients $G_{kk}(t)$ contain all the information about the perturbing interaction. Assuming only static quadrupole interaction with axial symmetry, the perturbation coefficient can be expressed by

$$G_{kk}(t) = \sum_{n=0}^{3} \sigma_{kn} \cos(n\omega_0 t) e^{\delta n \omega_0 t/2} , \tag{3}$$

where the frequency ω_0 is related to the nuclear quadrupole frequency, $\nu_Q = (10/3\pi)\omega_0$. The term $e^{-\delta n \omega_0 t/2}$ gives the Lorentzian distribution of frequencies having a width δ.

Since the A_{44} coefficient for the 173–247-keV sequence in ^{111}Cd is very small, we have assumed its value equal to zero and the experimental $G_{22}(t)$ parameter was extracted from the intensity ratio

$$\epsilon(t) = 2\frac{C(180°,t) - C(90°,t)}{C(180°,t) + 2C(90°,t)} = A_{22} G_{22}(t) , \tag{4}$$

where the detected coincidence intensity $C(\theta,t)$ is given by

$$C(\theta,t) = C_0 e^{-t/\tau W(\theta,t)} , \tag{5}$$

and where τ is the lifetime of the nuclear level.

The data were analyzed assuming that a part a_h of the probe nuclei is subjected to a high-frequency interaction ν_Q^h, a second part a_l is subjected to a distribution of low frequencies centered at ν_Q^l, and a third part a_0 of unperturbed probe nuclei does not feel any hyperfine field. This means that the experimental perturbation factors were fitted to a function of the form

$$G_{22}(t)_{\text{expt}} = a_0 + a_l G_{22}(\nu^l, t) + a_h G_{22}(\nu^h, t) , \tag{6}$$

where the G_{22} factors are given by expression (3) and $a_0 + a_l + a_h = 1$.

III. EXPERIMENTAL RESULTS

The temperature dependence of the observed quadrupole interactions in the cubic Ag matrix doped with impurities can be affected by three main factors: the mass M of the impurity, the valence difference ΔZ between host and solute,

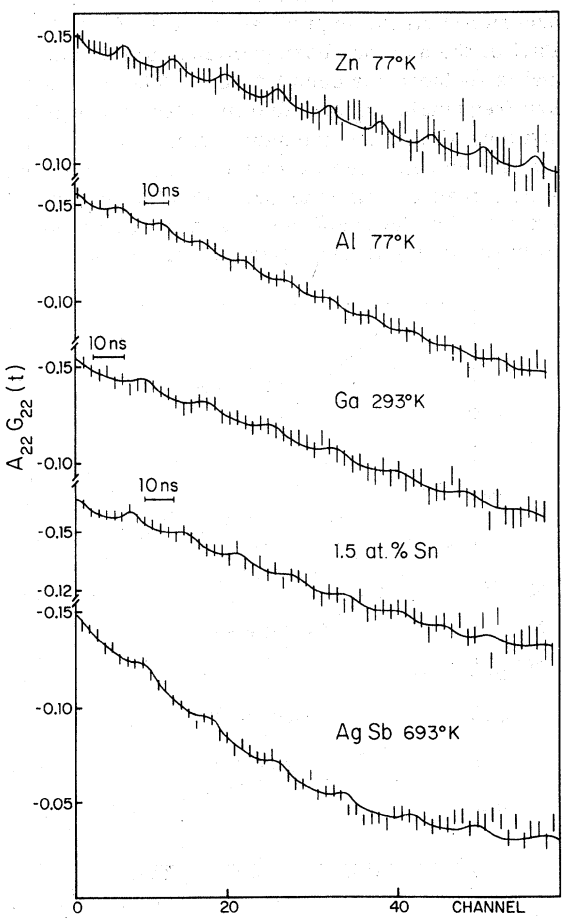

FIG. 1. $A_{22} G_{22}(t)$ curves for several impurities in Ag host.

and the impurity concentration. To investigate these factors, different impurities were used (Au, Cu, Zn, In, Sn, Sb, Al, and Ga); and for the Sn impurity, and the concentration was changed.

Typical results are shown in Fig. 1. The $A_{22}G_{22}(t)$ curves show very clearly that the ^{111}Cd nuclei are exposed not only to a smeared-out low-quadrupole frequency, but in addition, a certain percentage of them experienced a sharp high-quadrupole frequency denoted by the small peaks superimposed on the gradually declining curves. The sharp frequency is associated with the hyperfine field produced by nn to the probe nucleus. The low-frequency distribution is due to impurities occupying sites at various different atomic distances from the probe nuclei. Table I displays the values obtained for the high- and low-frequency interactions.

The temperature dependence of the sharp quadrupole frequency ν_Q^h is plotted in Fig. 2 as a function of $T^{3/2}$ for several impurities. As can be observed in all the cases the relation $\nu_Q^h(T) = \nu_Q^h(0)(1 - \alpha_h T^{3/2})$ is very well fulfilled. The same fact occurs for all the impurities listed in Table I. Part of the data has been published previously[6] and is included for completeness. The obtained low frequencies ν_Q^l are also included in Table I, and they also follow the same relation (1), despite the fact that in some cases the large experimental errors masked that evidence. Finally, in Table I, are included the coefficients α_l and α_h obtained from the fitting to the experimental points.

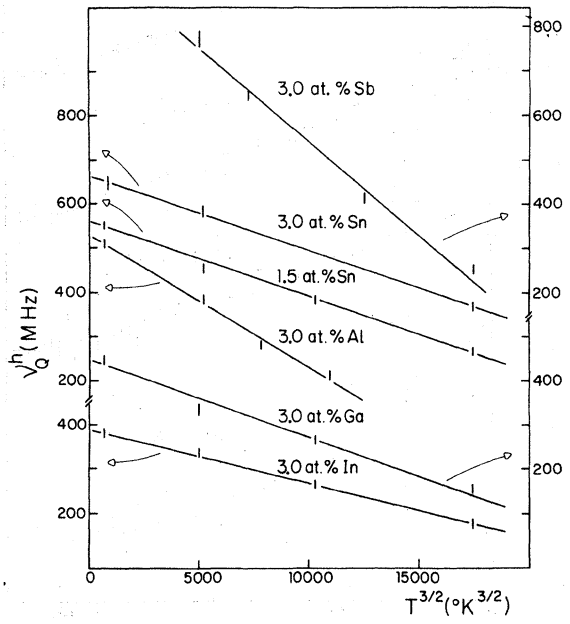

FIG. 2. Temperature behavior of the high-frequency interaction ν_Q^h for different Ag-base solid solutions..

An inspection of Table I shows that both α_h and α_l coefficients are dependent on the charge difference ΔZ between host and impurity, the mass of the impurity M, and the impurity concentration. In order to study individually these effects, we have classified the alloys in the following way.

(i) *Impurity mass effect*: The impurities of In, Ga, and Al have the same $\Delta Z = 2$ with respect to the host. Their atomic masses M are 115, 69, and 27, respectively. Table I shows that for both the high- and the low-frequency interaction, the coefficient α is strongly dependent on M. We adjusted the α_h values to a function of the form $\alpha_h = c/M^n$ (see Fig. 3). As can be observed in this log-log plot, a straight line fits the experimental points very well. The extracted slope is $n = 0.37 \pm 0.04$. Figure 3 also shows the α_l values as 2 function of M. Again, a straight line fits the experimental data, with a slope $n = 0.9 \pm 0.4$.

(ii) *Concentration effect*: For the Sn impurity, the E.F.G as a function of T was measured for two different concentrations, 1.5 and 3 at.%. The corresponding results are shown in Table I. As can be observed for the high-frequency interaction—Fig. 2—both lines show a striking parallelism reflected by the unnormalized slope values: $\nu_Q^h(0)\alpha_h(1.5\%) = (157 \pm 3) \times 10^{-4}$ and $\nu_Q^h(0)\alpha_h(3\%) = (161 \pm 9) \times 10^{-4}$ MHz °K$^{-3/2}$. Nothing definite can be said about the low-frequency slopes, basically due to the large experimental errors.

(iii) *Difference of charge effect*: At the same atomic concentration—3 at.%—six different alloys were measured; *Ag*Au, *Ag*Cu, *Ag*Zn, *Ag*In, *Ag*Sn, and *Ag*Sb, with Z ranging from 0 to 4.

Considering the EFG generated by nn impurities, it is interesting to note that for $\Delta Z = 0$ the corre-

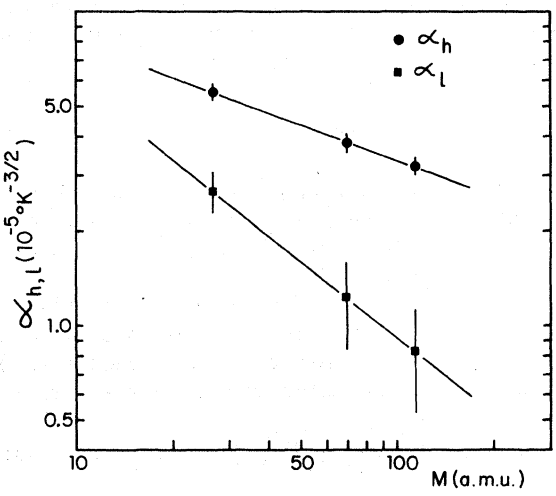

FIG. 3. α_h and α_l coefficients as function of M in a log-log plot.

TABLE I. Quadrupole frequencies ν_Q and α coefficients for ^{111}Cd in Ag-base solid solutions.

Impurity	Temperature (°K)	ν_Q^h (MHz)	α_h (10^{-5} °$K^{-3/2}$)	ν_Q^l (MHz)	α_l (10^{-5} °$K^{-3/2}$)
Cu	77	133 ±4		5.5 ±0.5	
$\Delta Z=0$	293	140 ±4	<10^{-2}	5.7 ±0.4	0.5 ±0.5
$M=63.54$	473	125 ±4		6.0 ±0.3	
3.0 at.%	673	137 ±4		5.2 ±0.5	
Au	77	29.9±0.9		3.5 ±0.7	
$\Delta Z=0$	293	28.7±0.5	<0.25	3.0 ±1.0	3.15±1.4
$M=196.97$	473	30.2±0.5		2.4 ±0.5	
3.0 at.%	673	28.1±0.5		1.4 ±0.5	
Zn	77	296 ±5		4.71±0.53	
$\Delta Z=1$	293	170 ±5		4.88±1.59	
$M=65.37$	323	165 ±5	7.6±0.8	2.32±0.42	6.2 ±2.0
3.0 at.%	373	139 ±5		1.13±0.50	
	423	112 ±5		2.86±0.65	
Al	77	507 ±8		5.2 ±0.3	
$\Delta Z=2$	300	382 ±6	5.5±0.3	5.0 ±0.3	2.68±0.4
$M=26.98$	393	279 ±4		3.8 ±0.3	
3.0 at.%	493	212 ±6		4.0 ±0.3	
Ga	77	445 ±8		6.1 ±0.5	
$\Delta Z=2$	293	334 ±16	3.8±0.2	4.5 ±1.0	1.24±0.4
$M=69.72$	473	263 ±11		5.5 ±0.5	
3.0 at.%	673	152 ±8		4.7 ±0.5	
In	77	379 ±7		8.2 ±0.5	
$\Delta Z=2$	293	333 ±5	3.2±0.2	6.7 ±0.7	0.83±0.3
$M=114.82$	473	265 ±8		6.4 ±0.6	
3.0 at.%	673	173 ±5		7.0 ±0.5	
Sn	77	550 ±10		8.5 ±0.5	
$\Delta Z=3$	300	456 ±10	2.9±0.1	8.3 ±0.3	1.12±0.53
$M=118.69$	473	384 ±6		7.6 ±0.3	
1.5 at.%	673	267 ±6		7.0 ±0.3	
Sn	90	643 ±16		10.3 ±0.3	
3.0 at.%	300	583 ±14	2.6±0.3	10.5 ±0.3	0.34±0.25
	673	366 ±11		9.8 ±0.3	
Sb	293	766 ±21		11.7 ±0.4	
$\Delta Z=4$	373	639 ±11	4.2±0.4	11.9 ±0.4	2.35±0.5
$M=121.75$	540	406 ±11		9.3 ±0.3	
3.0 at.%	673	252 ±8		8.2 ±0.4	

sponding temperature slopes α_h(Au) and α_h(Cu) are consistent with zero. This fact indicates that it is essential to have a difference of charge in order to get a high-frequency variation with the temperature. In addition, an inspection of Table I shows that α_h is strongly dependent on ΔZ. The α_h dependence of ΔZ is shown in Fig. 4 for Zn, In, Sn, and Sb impurities.

Assuming that the M^{-n} dependence on α_h also applies to elements situated in different columns of the periodic Table, we have corrected the α_h values. The new values also show a strong dependence on ΔZ. However it is very hard to extract an empirical relation from the present results.

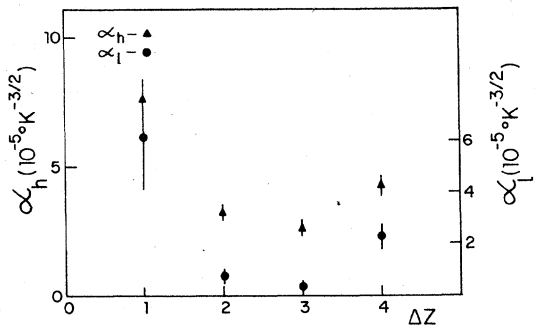

FIG. 4. α_h and α_l as a function of ΔZ, the difference of valence between the impurity and Ag.

A similar situation occurs with α_l. In Fig. 4 are also represented α_l vs ΔZ, and as can be seen, there is a strong dependence on ΔZ. As in the previous case, a mass correction does not help to draw any further conclusion.

IV. CONCLUSIONS

The present is the first work where the temperature dependence of the EFG generated by impurities in a cubic Ag matrix have been systematically studied. The basic parameters were changed, and their influence on the temperature behavior have been analyzed. As a consequence, several conclusions can be drawn from the present results.

(i) The EFG created by both the nn and the distant impurities in a cubic Ag matrix are dependent on the temperature, following the relation

$$\nu_Q(T)=\nu_Q(0)(1-\alpha T^{3/2}),$$

that is, a relation similar to the one obtained for almost all the noncubic systems.

(ii) For $\Delta Z=0$, the high-frequency slope α_h is consistent with zero for two different impurities (Cu and Au), while for the other ΔZ values α_h not only is different from zero, but is ΔZ dependent. However, the obtained results do not allow us to draw any further straightforward conclusion, since they do not follow any simple relation. Probably competitive effects are taking place, masking the ΔZ dependence. It is well known that besides the valence effect, there is a considerable contribution of the size effect (strains caused by atomic misfit of the impurity) to the EFG in doped cubic metals.[7,8] However, for the case of Cu impurity, where the EFG is due mainly to the size effect,[8] we observe a very small temperature dependence. This would indicate that the strains produced by the impurity have a small effect on the temperature behavior of the EFG.

(iii) Both α_l and α_n slopes show a definite strong mass effect at variance with what seems to happen in pure noncubic metals, where contradictory results have arisen.[2,4] A semiquantitative approach could be done in order to explain the mass dependence of the α slope in a doped cubic metal. Nishiyama *et al.*[3] write the temperature dependent EFG for noncubic systems in the form

$$_{eq}(T)=(1-\gamma)\,eq_{ion}^{sc}(T)\exp(-\tfrac{1}{2}k_F^2\langle u^2\rangle)\,. \qquad (7)$$

In order to apply this expression to cubic systems doped with impurities, we have to take into account that: (a) $\langle u^2\rangle$ is the mean-square value of the lattice displacements at the impurity site because it is the impurity that generates the EFG at the probe site. This means that the phonon modes of the impurity-plus-lattice system have to be considered in order to evaluate the Debye-Waller factor $e^{-k_F^2\langle u^2\rangle/2}$. These kinds of calculations were already performed by Kagan and Iosilevski[9] when they evaluated the probability of the Mössbauer effect at the impurity site. (b) According to Nishiyama *et al.*, the eq_{ion}^{sc} term is only a function of the temperature-dependent lattice parameters. Then one can assume that this term does not depend on the impurity mass, leaving, therefore, all the mass dependence of the EFG to the $\langle u^2\rangle$ term in relation (7).

We have calculated $\langle u^2\rangle$ at constant temperature [(following Ref. (9))] as a function of $\epsilon=1-M/m$, M being the impurity mass, and m the mass of the matrix. The assumptions made in order to perform this calculation are (a) we have neglected impurity size effects and impurity-probe interactions. (b) In the expression (7) we have approximated $e^{-k_F^2\langle u^2\rangle/2}$ by $1-\frac{1}{2}k_F^2\langle u^2\rangle$. This approximation is valid only for a restricted range of temperature. The results are shown in Fig. 5, where $\alpha(\epsilon)$ (in arbitrary units) represents the α dependence on the impurity mass. (Details of the calculations will be published elsewhere.) Despite all the approximations, the normalized calculated curve follows fairly well the trend of the experimental α_h values (for a wide range of impurity masses), indicating that the above mentioned assumptions are reasonable.

The low-frequency slope α_l also has a strong M dependence; however, the large experimental errors preclude any definite comment.

(iv) The fact that the temperature behavior of the EFG created by nn is independent of the impurity concentration (in the range 1.5 to 3 at.%) shows that the impurity-impurity interaction is negligible. Then, each impurity keeps its own mode of oscillation, the phonon spectrum remaining the same, as the concentration is changed.

(v) In the measurements done on noncubic met-

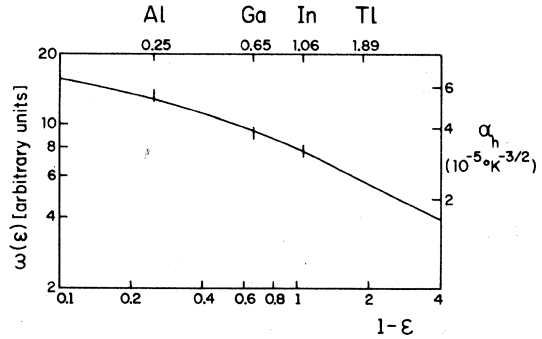

FIG. 5. The theoretical mass dependence of α_h (solid line) as a function of the ratio M/m, the mass of the matrix remaining constant. The bars represent the experimental α_h values.

als[1] the obtained values of α are of the order of 10^{-5} $^{\circ}K^{-3}$ [2], which is of the same order of magnitude as those measured in the present experiment for $\Delta Z \neq 0$.

ACKNOWLEDGMENTS

The authors want to acknowledge Dr. C. Scherer and Dr. N. Rivier for fruitful discussions.

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*Work supported in part by Conselho Nacional de Desenvolvimento Científico e Tecnológico and Financiadora de Estudos e Projetos.

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