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Temperature Dependence of the Electric Field Gradient in Cubic Ag Metal Doped with Impurities*

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The electric quadrupole interactions produced by near-neighbor impurity atoms of Cu, Zn, In, Sn, and Au in a cubic Ag metal lattice are measured as a function of temperature by the time-differential perturbed angular correlation method. The obtained electric quadrupole frequencies ω can be reproduced by the relation $\omega(T) = \omega(0)(1 - \alpha T^{3/2})$ with a strong dependence of the coefficient α on the impurity atom. The results are discussed in terms of recently proposed models to explain the $T^{3/2}$ dependence.

The temperature dependence of electric field gradients (EFG's) has been measured for several noncubic metals such as Zn and Cd (hexagonal), Sn and In (tetragonal), and β -Ga (monoclinic). An analysis of these results shows that the quadrupole frequency $\omega_Q = eQV_{zz}/\hbar$ at the nuclear sites is well reproduced by a $T^{3/2}$ relation.¹

It has been known for many years that when an impurity atom is introduced into a cubic metal,

the cubic symmetry is destroyed and nuclei near the impurity experience EFG's. These fields are generated by the valence difference between host and solute and by lattice strains (size effects). In general any disturbance in the periodicity of the lattice gives rise to a redistribution of conduction electrons around the solute and consequently creates an EFG. This subject has been extensively studied by NMR techniques,²⁻⁵ and

more recently was also investigated by the time-differential perturbed-angular-correlation (TDPAC) method.^{6,7}

In this paper we use the TDPAC to study the temperature dependence of quadrupolar interactions in the cubic Ag host doped with Cu, Zn, In, Sn, and Au impurities. Although the Sn data have been presented previously,⁷ they are included in this paper for completeness. The radioactive probe nuclei were produced by the reaction $^{109}\text{Ag}(\alpha, 2n)^{111}\text{In}$ where the ^{111}In nuclei decay to ^{111}Cd by electron capture. We measured the interaction of the quadrupole moment Q of the 247-keV nuclear state, lifetime $\tau = 120$ ns, in Cd with the EFG's produced by the impurities. The impurities (3 at.%) were introduced into Ag by melting the constituents (with purity $\geq 99.99\%$) under argon atmosphere and annealing the alloys, also in argon, for 2 h. This means that our samples contain three components: the host, Ag; the impurity solute atoms; and the very dilute radioactive probe nuclei of ^{111}In .

The TDPAC factors $G_{kk}(t)$ contain the quadrupole interaction frequencies. For randomly oriented static EFG's V_{zz} with axial symmetry, these factors are given by the expression

$$G_{kk}(t) = \sigma_{k0} + \sum_{n=1}^3 \sigma_{kn} \cos(n\omega_0 t) \exp(-\frac{1}{2}\delta n\omega_0 t), \quad (1)$$

where for $I = \frac{5}{2}$, $\omega_0 = 3eQV_{zz}/20\hbar$. The term $\exp(-\frac{1}{2}\delta n\omega_0 t)$ gives the Lorentzian distribution of frequencies having a width δ . Characteristic spectra for Au and Zn impurities at different temperatures are shown in Fig. 1. The shape of the $G_{22}(t)$ curves reflects a distribution of EFG's with a sharp frequency superimposed on the gradually declining curves. The full lines in the curves are computer fits, assuming that a part of the probe nuclei are subjected to a high-frequency interaction ω_0^h and a second part to a distribution of low frequencies centered around ω_0^l , while a third part consists of unperturbed probe nuclei, which do not feel any hyperfine field. The sharp frequency is associated with the hyperfine field produced by an impurity-atom nearest neighbor to the probe nucleus. The distribution of low frequencies 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 frequencies.

The temperature dependence of the sharp quadrupolar frequencies ω_0^h is plotted in Fig. 2 as a function of $T^{3/2}$ for the five impurities. These results are for the same concentration of solute

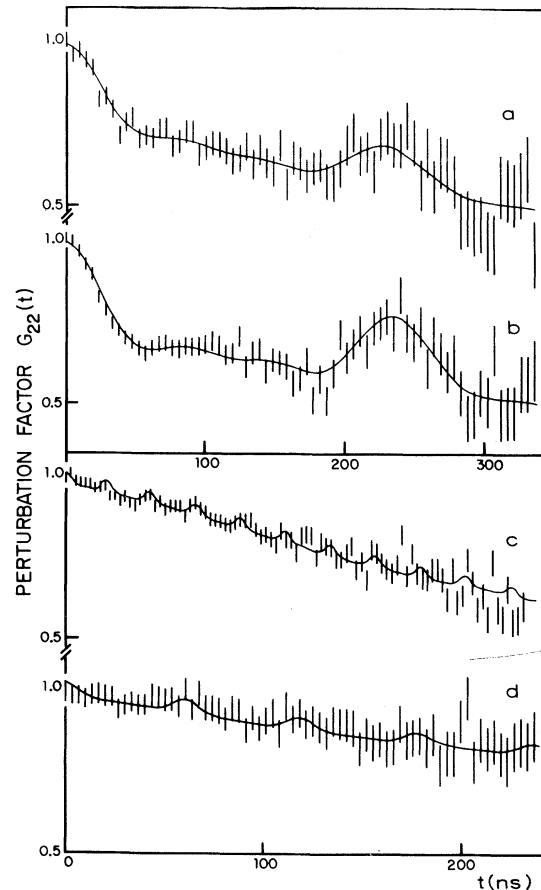


FIG. 1. $G_{22}(t)$ perturbation factor; curves a and b for Au impurity at 293 and 673°K; curves c and d for Zn impurity at 77 and 423°K.

(3 at.%) and show that there is a drastic effect of the impurity on the slope of the temperature dependence. Heubes *et al.*⁸ first suggested the relation

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

to explain the measured temperature variation of the quadrupole frequency in noncubic metals.

The full lines in Fig. 2 are fittings using expression (2) for the quadrupole frequency, giving for the constant α the values $< 10^{-7}$, $< 2.5 \times 10^{-6}$, $(2.5 \pm 0.3) \times 10^{-5}$, $(3.2 \pm 0.3) \times 10^{-5}$, and $(7.6 \pm 0.5) \times 10^{-5}$ for Cu, Au, Sn, In, and Zn impurities, respectively.

Besides the differences in mass of the impurity there is a valence difference ΔZ between solute and solvent. For impurities of Cu and Au, both with $\Delta Z = 0$, and masses differing by a factor of 3, the quadrupolar interaction shows a very small temperature dependence. Large effects in the slope are observed in the case of Zn, In, and Sn

TABLE I. Quadrupolar frequencies obtained from the fitting of the experimental curves $G_{22}(t)$.

Impurity	Temperature (°K)	ω_O^h (MHz)	ω_O^l (MHz)
Cu	77	125 ± 4	5.2 ± 0.5
	293	132 ± 4	5.4 ± 0.4
	473	118 ± 4	5.7 ± 0.3
	673	129 ± 4	4.9 ± 0.5
Au	77	28.2 ± 0.9	3.3 ± 0.7
	293	27.1 ± 0.5	2.8 ± 1.0
	473	28.5 ± 0.5	2.3 ± 0.5
	673	26.5 ± 0.5	1.3 ± 0.5
Zn	77	279 ± 5	4.44 ± 0.50
	293	160 ± 5	4.60 ± 1.50
	323	156 ± 5	2.19 ± 0.40
	373	131 ± 5	1.07 ± 0.47
	423	106 ± 5	2.70 ± 0.60
In	77	357 ± 7	7.7 ± 0.5
	293	314 ± 5	6.3 ± 0.5
	673	163 ± 5	6.6 ± 0.5
Sn	90	606 ± 15	9.7 ± 0.3
	300	550 ± 10	9.9 ± 0.3
	673	345 ± 10	9.2 ± 0.3

impurities; for Zn ($\Delta Z=1$) the constant α in Eq. (2) is 3 times larger than for Sn ($\Delta Z=3$) and 2.4 times larger than for In ($\Delta Z=2$). The mass of Zn is smaller than that of Ag, and In and Sn have masses of the same order as Ag. These results show that the temperature behavior of the EFG's generated by an impurity cannot be explained in a straightforward way purely from the consideration of ΔZ and/or differences in mass of the impurities.

The recently proposed theories to explain the $T^{3/2}$ dependence of the EFG^{9,10} are for pure metals only and do not apply directly for the kind of alloys studied here. Nevertheless it is interesting to comment briefly about the approaches used. Jena⁹ considers the interaction of the conduction electrons with the phonons of the lattice and deduces a $T^{3/2}$ dependence of the EFG in noncubic metals. The calculation is made in the Debye-Waller model, and the main conclusion is that the conduction electron part is largely responsible for the T dependence of the EFG. As our data show large effects only for impurities with valence different from that of the host, the observed

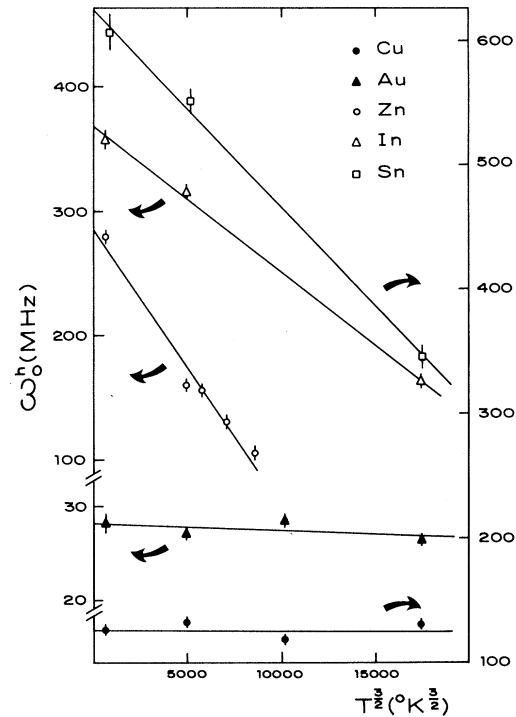


FIG. 2. Temperature dependence of the quadrupole interaction frequency plotted against $T^{3/2}$ for impurities of Cu, Zn, In, Sn, and Au.

slopes could be correlated to the T dependence of the conduction-electron screening of the excess charge in the vicinity of the solute. An extension of the model for the systems investigated in this paper is desirable.

In a similar approach Nishiyama *et al.*¹⁰ successfully fitted the $T^{3/2}$ behavior in noncubic metals, including explicitly the effect of the host lattice vibrations, with the main contribution being from the variation of the Debye-Waller factor of the ions. As the host and the probe nuclei are the same in our samples, the observed different slopes could be correlated with local vibrations of impurities having different size, mass, and charge. An initial difficulty in this approach is that Cu and Au impurities with different masses show very similar effects, in spite of the fact that, as is known from Mössbauer measurements, there are differences in the T dependence of the Debye-Waller factor for light and heavy (relative to the host mass) impurity atoms.

Finally, there is the suggestion by Christiansen *et al.*¹ based on an interaction between neighboring atomic quadrupoles giving rise to elementary excitations in analogy to magnon excitation in a ferromagnet where a $T^{3/2}$ law of the magnetiza-

tion is derived. Our results cannot be explained within the framework of this approach, firstly, because we observe a strong $T^{3/2}$ dependence in a doped cubic metal where it is difficult to assume such an interaction; secondly, because we observe a correlation between the intensity of the quadrupole nuclear interaction and the strength of the temperature variation, characterized by the coefficient α , which is opposite to what should be expected in the proposed model.

We would like to add that the low-frequency distributions also display a temperature-dependent variation but because the errors are large we are not extracting definite conclusions.

In summary the present experimental results show that in a cubic metal doped with impurity a $T^{3/2}$ relation for the EFG is also observed and that the slope of this temperature dependence strongly depends on the valence and/or mass of the impurity.

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Electronic Excitations in LiF: 10–70 eV*

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In the past three years, a number of different interpretations of the optical properties of LiF have appeared in the physics literature. We present new evidence which shows that most of these interpretations are incorrect in the soft-x-ray region, and for the first time we present measurements of anisotropies in the excitations in the ultraviolet region as a function of momentum transfer in single-crystal samples.

LiF is often thought of as the “hydrogen atom” of the insulators: It has the simplest atomic constituents and therefore its electronic properties ought to be understandable at a basic level. Nevertheless, in spite of a continuing effort over the years, including much recent activity,^{1–8} there remain large gaps and discrepancies regarding its fundamental electronic excitations. In the present work, inelastic electron scattering spectra were obtained for LiF thin films using the Princeton inelastic scattering spectrometer.⁹ Samples were of two kinds: polycrystalline thin films evaporated onto a thin Formvar substrate, and single-crystal self-supporting films prepared by mechanical polishing followed by ion milling. In each case the films were exposed to air for a short period of time after preparation and before measurement. Film thicknesses used in the re-

sults reported here varied from 1000 to 3500 Å. The data presented in this Letter have not been corrected for multiple scattering, although such an analysis has been carried out and will be presented at a later date. With the exception of experimental values of oscillator strengths, the present discussion depends only on the shapes of features and not on absolute values of the response function. Two kinds of new experimental results are presented here:

Localized excitations.—The operator which causes excitations in inelastic electron scattering is¹⁰ $e^{i\vec{q}\cdot\vec{r}}$, where \vec{r} is the position of an electron and \vec{q} the transferred momentum. In the case of a localized initial state this operator may be expanded: $e^{i\vec{q}\cdot\vec{r}} = 1 + i\vec{q}\cdot\vec{r} + \frac{1}{2}(i\vec{q}\cdot\vec{r})^2 + \dots$. The first term does nothing since initial and final states are orthogonal; the second term, which