This resonance enhancement will be useful also with other materials to identify localized levels hidden in valence-band spectra. The spectra obtained here will be analyzed from this point of view elsewhere.

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# Anomalous Temperature Dependence of the Electric-Field Gradient at $^{181}$Ta Impurities in Holmium: Influence of Host 4*f* Crystalline-Field Levels

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Measurements of the electric quadrupole interaction at $^{181}$Ta impurities in paramagnetic Ho metal using time-differential perturbed angular correlations show marked deviation from the usual $T^{3/2}$ behavior. A phenomenological theory applied to this and other cases of closed-shell probes in rare-earth metals indicates that the deviation is due to the aspherical charge distribution of the *host* ion arising from the influence of the crystalline electric field on their unfilled 4*f* shells.

The temperature dependence of the electric-field gradient (EFG) in noncubic metals or alloys has been found to obey a $T^{3/2}$ relation.[1] This is now generally believed to be associated primarily with temperature-dependent lattice vibrations of the host atoms which are mediated to the probe atoms by the conduction electrons.[2-4] In this Letter we present the first unambiguous observation of a deviation from the $T^{3/2}$ law in a normal alloy not involving incomplete electronic shells of

 

the probe atoms (which will produce a local EFG), and not involving abnormal lattice locations.[1,2] An explanation for the deviation is provided which has general applicability to a large number of possible systems. We have studied the dilute alloy system *Ho*Ta in the paramagnetic temperature range using time-differential perturbed angular correlation (TDPAC)[5] in the decay of $^{181}$Hf to $^{181}$Ta. In this system, the metallurgy is simple and the probe atom has fully occupied electron shells. However, the unusual feature here in comparison with other such experiments is that the host material consists of rare-earth ions with incomplete $4f$ shells. Comparison of our results with the structurally similar system *Lu*Ta, where the host atoms have a closed $4f$ configuration, shows that the observed deviations arise because crystal-field interactions which are present in the *host* atom are reflected in the EFG at the probe.

The dilute (6000 at. ppm) *Ho*Hf alloy samples were prepared by melting together appropriate quantities of 99.9% pure holmium metal and 99.999%-pure hafnium metal in an argon arc furnace. The 43-d $^{181}$Hf parent of the probe was produced by thermal-neutron irradiation either of the Hf starting material or of the finished alloy, in different samples. The TDPAC data were taken in a three-NaI(Tl)-detector time-and-angle spectrometer. The hyperfine interaction between the EFG and the electric-quadrupole moment of the $^{181}$Ta nucleus perturbs the angular correlation of the well-known 133–482-keV $\gamma$-$\gamma$ cascade. The corresponding static attenuation coefficient $G_2(t)$ for a polycrystalline sample is deduced from the measurement of coincidence rates between the two $\gamma$ rays at angles of 90° and 180°. For the present case[6] where the intermediate-state nuclear spin $I=\frac{5}{2}$,

$$G_2(t)=\sum_{n=0}^{3} a_n \exp[-\tfrac{1}{2}(\delta\omega_n t)^2]\cos(\omega_n t). \quad (1)$$

Here $\omega_1=3\pi\nu_Q/10=\omega_3-\omega_2$, and the parameter $\delta$ indicates the degree of distribution in the magnitude of the EFG, assuming that distribution to be Gaussian. The quadrupole interaction frequency $\nu_Q=e^2qQ/h$, where $Q$ is the nuclear quadrupole moment and $eq$ is the largest component of the EFG tensor in the principal-axis system. The coefficients $a_n$ were allowed to vary in the least-squares fitting routine in order to allow for the incomplete randomness of the crystallites in the arc-melted samples.

The experiment was run at eleven temperatures between 140 and 701 K. Typical data are shown in Fig. 1. The experimental $G_2(t)$ show a single axially symmetric electric-quadrupole interaction over the entire measured temperature range. There is a small temperature-independent distribution of the EFG magnitude. Our value of $\nu_Q$ at room temperature, 395.9(14) MHz, is slightly lower than the value of Forker, Fechner, and Haverkamp[7] of 408(8) MHz. However, those authors saw a marked EFG asymmetry in their samples of several rare-earth metals, and concluded that some of their probe atoms were not in regular lattice sites. The absence of any asymmetry in our samples, and the insensitivity of the measured frequencies to thermal cycling, is evidence that the probe nuclei occupy regular sites in the hcp Ho lattice in the present case.[8]

The dependence of the measured quadrupole frequency on $T^{3/2}$ is shown in Fig. 2, and compared with that previously obtained for Ta in Lu metal by Butz and Kalvius.[9] It is apparent that the EFG in the present case deviates strongly from a $T^{3/2}$ dependence at the low temperatures. This is in contrast to the structurally similar case of *Lu*Ta, which displays the $T^{3/2}$ behavior observed in all other metallic systems not involving either open orbitals of the *probe* ion or irregular lattice sites. The only possible exception previously observed[10] was for *Tm* Yb; however, in that case the accuracy of the data was such that the deviations were not well established. Nonetheless, we should note that in both *Ho*Ta and *Tm* Yb, the probe ions have filled shells,[11] whereas the host ions have open $4f$ orbitals. As a result, the host ions have an aspherical charge distribution at temperatures smaller than the total crystalline-electric-field (CEF) splitting.

Effects from such aspherical charge distribu-

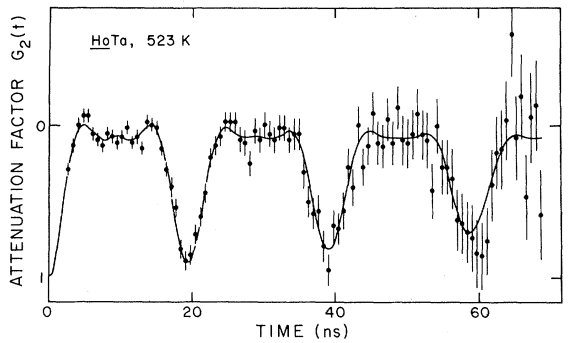


FIG. 1. Typical measured attenuation factor $G_2(t)$ for $^{181}$Ta in Ho metal. The solid line represents a least-squares fit of Eq. (1) to the data.

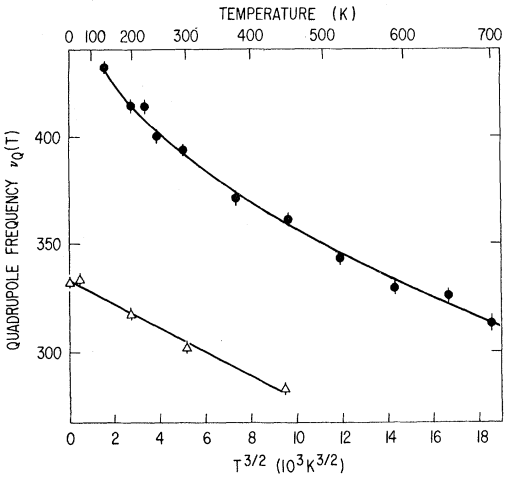


FIG. 2. Dependence of the quadrupole interaction frequency on $T^{3/2}$. Open triangles refer to *Lu*Ta (Ref. 9) and closed circles to *Ho*Ta. In both cases, the solid line represents a least-squares fit to Eq. (5).

tions about rare-earth ions have been previously seen in electrical and thermal conductivity measurements,[12] and most clearly in magnetoresistance studies.[13-15] In all these cases, unusual temperature dependences and/or anisotropies are observed which can be explained by Coulomb scattering of the conduction electrons from the quadrupolar charge distributions of the $4f$ electrons. In a simple point-charge calculation of the lattice contribution to the EFG, such asphericity is not considered. We suggest that, in cases such as those presently being considered, such as approximation is not valid, and that the nonspherical charge distribution on the host ions may be experienced by the probe atom.

Nishiyama and Riegel[4] have recently discussed the analysis of electric field gradients in metallic systems. Within certain approximations it is shown that the EFG can be written

$$eq = (1-\gamma_{\rm eff})eq_{\rm ion}^{\rm sc}\exp[-\tfrac{4}{3}k_{\rm F}^2\langle u^2\rangle], \qquad (2)$$

where $\gamma_{\rm eff}$ is a shielding factor and $eq_{\rm ion}^{\rm sc}$ is the EFG arising from the screened charge of the neighboring ions. The last factor is essentially a Debye-Waller factor with $k_{\rm F}$ the Fermi momentum for the conduction electrons in the material and $\langle u^2\rangle$ the mean-square displacement for the neighboring ions. The product of the relatively weak temperature dependence of $q_{\rm ion}^{\rm sc}$ due to the lattice expansion and the rather large change with temperature due to the Debye-Waller factor yields the observed $T^{3/2}$ dependence. For the present case it is necessary to reconsider the term $eq_{\rm ion}^{\rm sc}$. This is given by

$$eq_{\rm ion}^{\rm sc} = \textstyle\sum_i 2V_2(r_i)P_2(\cos\theta_i), \qquad (3)$$

where $V_2(r_i)$ is the second derivative of a Coulomb potential due to the neighboring ions, and the sum runs over all other sites in the lattice. If $V_2(r_i)=Ze/r_i^3$, this reduces to a traditional point-charge calculation. For finite, spherically symmetric ions, Eq. (3) must also include explicitly the radial dependence of $V_2(r_i)$. This affects the absolute magnitude of $eq$, but introduces no temperature-dependent factors which are not already included in principle in the point-charge calculation. For cases such as the present one, the neighboring ions are not spherically symmetric, which introduces additional modifications in the screened potential. Furthermore, these modifying terms will be temperature dependent as a result of the change in the charge distribution with changing occupation of the CEF levels.

Since the physical mechanism by which the aspherical host charge distribution affects the EFG at the probe nucleus is not known in detail, we give here a phenomenological discussion. We consider the changes due to asphericity to be relatively small so that they can be included by a low-order expansion of the EFG due to the screened potential. The first term of such an expansion will be that obtained for spherically symmetric ions. We consider the second term of the expansion to be directly related to the electronic quadrupole moment of the host ions, and hence proportional to $\langle 3J_z^2 - J^2\rangle_T$, where $J$ is the angular momentum of the ground multiplet of the host ion and $\langle\ \rangle_T$ represents the quantum-mechanical and thermal average over all CEF states. Thus,

$$eq_{\rm ion}^{\rm sc} = eq_{\rm ion}^{0}(1 - C\langle 3J_z^2 - J^2\rangle_T). \qquad (4)$$

Combining the various results discussed above we then obtain

$$eq(T) = A(1 - BT^{3/2})(1 - C\langle 3J_z^2 - J^2\rangle_T). \qquad (5)$$

The solid line in Fig. 2 gives the results of a least-squares fit of Eq. (5) to the *Ho*Ta data, using the Ho CEF parameters of Touborg.[16] One sees that the observed temperature dependence can be easily reproduced. A similar analysis has been successfully applied to the *Tm*Yb data. The values for the constants $A$, $B$, and $C$ of Eq. (5) are listed in Table I for these two systems as well as for *Lu*Ta. In the last case, of course, the constant $C$ is zero since CEF effects are not present because of the closed-shell configuration of

TABLE I. Coefficients giving the temperature dependence of the EFG according to Eq. (5). Experimental data were obtained from measured $\nu_Q$ using nuclear quadrupole moments $Q(^{181}\mathrm{Ta}) = 2.51$ b (Ref. 17) and $Q(^{172}\mathrm{Yb}) = 2.7$ b (Ref. 10).

| System | $A$ ($10^{17}$ V/cm$^2$) | $B$ ($10^{-5}$ K$^{3/2}$) | $C$ |
|---|---|---|---|
| *Ho*Ta | 6.5 | 1.2 | +0.048 |
| *Tm*Yb | 5.1 | 1.7 | −0.027 |
| *Lu*Ta | 5.5 | 1.5 | 0 |

Lu.

A detailed evaluation of the parameters in Table I requires a complete theoretical formulation of the above phenomenon. However, certain general characteristics may be noted. The point-charge contribution to the EPG, which is carried by the constants $A$ and $B$, should be approximately the same in all hosts; this is seen to be the case. The constant $A$ may be expected to show some variation since the probe ion (and thus $\gamma_{\mathrm{eff}}$) is different in the case of *Tm*Yb. The constant $B$ is determined primarily by lattice-dynamical properties of the host, and so should show little variation among all three cases. Again, this is found to be true. The coefficient $C$ reflects the coupling of the quadrupolar term from the host. The fact that this is of the same order of magnitude for the two systems with incomplete $4f$ shells indicates that crystal-field effects are entering in a comparable way for both cases. In a complete theory of this effect, the coefficient $C$ would depend on the mechanism by which the charge distortion on the host atom affects the EFG seen at the impurity nucleus. The magnitude of the contribution to the potential at the probe atom due to the quadrupolar deformation of the rare-earth ion may in itself be small; however, it is subject to shielding or antishielding by the intervening electrons. This may include both simple screening effects by all the electrons present, reflecting the charge distribution of the rare-earth ion, as well as the production of an EFG which is more directly transferred to the probe atoms by the nonspherical $5d$ conduction electrons.

Systematic deviations from the otherwise universal $T^{3/2}$ temperature dependence of the EFG have thus been found in rare-earth metals even when the probe atom has a closed-shell configuration. These deviations are shown to arise from the temperature-dependent nonspherical charge distribution due to the open $4f$ orbitals of the host atoms. The model presented here is successful in providing a framework for the consideration of these effects. It is hoped that these results will stimulate more detailed theoretical calculations in order to understand more fully the mechanism by which host charge distortion affects the EFG in such cases.

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