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Temperature Anomalies of Hyperfine Fields of *s-p* Impurity Elements in Cobalt

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The hyperfine magnetic field H_{hf} at extremely dilute impurities of Ga, Ge, and As in a single crystal of hcp Co has been measured as a function of the temperature T up to $T \cong 900$°K. The functions $H_{hf}(T)$ exhibit dramatic differences for these adjoining elements; while $H_{hf}(T)$ in As*Co* scales with the hcp host magnetization $\sigma(T)$, $H_{hf}(T)$ in Ga*Co* decreases much faster than $\sigma(T)$ and $H_{hf}(T)$ in Ge*Co* *increases* by ~25%. This is the first observation of an increase with temperature of the magnitude of the hyperfine field at an impurity atom in any ferromagnetic metal.

It is well known that the systematics of hyperfine fields H_{hf} at dilute nonmagnetic impurities in 3*d* ferromagnets exhibit striking variations with the impurity charge number Z. The sign of H_{hf} reverses from negative to positive regularly at the middle of the *s-p* series of each period, e.g., near Ge (4*sp*) and near Sn (5*sp*). Although these systematics have been studied for over a decade, a complete understanding is still lacking. It is believed that these sign reversals of H_{hf} result from competition between conduction-electron polarization (CEP) and overlap-exchange polarization of the valence *s*-like electrons of the impurity, but the physical origins of these contributions, especially the latter, remain controversial.[1] Direct experimental information on the components that make up H_{hf} is scarce and not easy to obtain. From this point of view, the impurities immediately around the point of sign crossover of H_{hf} (e.g., Ge or Sn) for which the different contributions compete nearly equally and produce a small net field are particularly interesting. In these cases, differences between the temperature dependence of those components sensitive to radial dependence or volume effects, and that of the CEP which is expected to scale roughly as the host magnetization $\sigma(T)$, could produce large effects in the observed $H_{hf}(T)$. Indirectly, this could lead to important insight into the origin of these hyperfine fields.

Experimental data on $H_{hf}(T)$ are available for *sp* impurities, mainly for an Fe host.[2] These show that although small deviations of the order of several percent from the reduced magnetization of the host $\sigma(T)/\sigma(0)$ are commonly observed, it is not possible to draw clear conclusions on the origin of these effects. On the other hand, $H_{hf}(T)$ for Sn in Co, which is located at the sign crossover of H_{hf} of the 5*sp*-series impurities, is known to be strikingly anomalous.[3] This anomaly is thought to be due to the influence of thermal vibrations on the overlap contribution to H_{hf}.[3] This is, however, not completely established and furthermore the Sn*Co* anomaly remains so far the only one of its kind. It is therefore interesting to investigate whether it is an isolated case or whether similar anomalies are present systematically for the isoelectronic 4*sp* impurities in a Co host.

In this Letter, we report measurements of $H_{hf}(T)$ in the range $T = 77$ to 900°K for Ga, Ge, and As impurities (concentration ~10^{-10}) in a single crystal of Co. Our results show that the temperature dependences of the hyperfine field at these adjacent impurities are dramatically different. For As, $H_{hf}(T)$ follows closely the host magnetization $\sigma(T)$ in the hcp phase; for Ga, $H_{hf}(T)$ decreases much more rapidly than $\sigma(T)$, while for Ge, $H_{hf}(T)$ displays a deviation from $\sigma(T)$ of the opposite kind, viz., it actually *increases* by about 25% in the temperature range studied. Considering that the host magnetization *decreases* by about 6% in this range, the Ge*Co* result is remarkable and represents the first

observation of an increase with temperature in the magnitude of the hyperfine field of any dilute impurity element in a ferromagnetic metallic host.

The systematic nature of the present results has been made possible by new and important advances in time-differential perturbed γ-ray angular distribution techniques accruing from the application of pulsed heavy ions. These techniques have been applied in the past to hyperfine interaction (HFI) studies using nuclear reactions induced by light ions (p, d, α, etc.).[4] However, such studies were often hampered by the limited choice of useful probes and by the fact that HFI could be studied only in the target material itself, limiting the choice also of the host materials. Compound-nuclear reactions induced by heavy ions such as ^{16}O are highly specific in exciting isomeric nuclear states with substantial cross sections. Because of the high angular momentum transferred, the excited isomer is also highly aligned. By using the right projectile at suitable energies, it is possible to excite probe nuclear states convenient for HFI studies in almost every element. The technique thus succeeds in providing a wide choice of isomeric probes for systematic probe-dependent studies of hyperfine fields. Because of the high projectile energies used in these reactions (~50 MeV), the activated isomer has large recoil energies available. This permits it to be recoiled out of relatively thick reaction targets into an independent host material. Thus, a clean separation of the nuclear and solid-state aspects of the experiment is achieved and host materials of unusual forms such as single crystals can be used routinely.

The experiments reported here were performed with a 53-MeV ^{16}O beam from the Rutgers-Bell tandem accelerator. The beam was pulsed with a repetition period of 1 μsec. A list of probe nuclear states and their production reactions used in the present work is given in Table I. Targets of the appropriate isotope in the form of metallic layers ~1 mg/cm^2 thick were clamped together with a single crystal of Co (dimensions 0.75 cm $\times$ 1 cm $\times$ 0.65 mm) in the hexagonal close-packed (hcp) phase. The reaction γ rays (see Table I) were detected by either a planar Ge(Li) crystal or a NaI(Tl) detector at $\pm 45^\circ$ to the beam axis. The c axis of the hcp Co crystal was oriented perpendicular to the reaction plane. An external magnetic field of 1.7 kOe was applied parallel to the c axis of the crystal. The time distributions of the γ-ray intensity after each beam burst, recorded by standard slow-fast electronics, were used to construct the standard ratio $R(t)$, the normalized difference in counting rates for the field directions "up" and "down." This yields $R(t) = A \sin 2\omega_L t$, where ω_L is the Larmor precession frequency. Typical precession patterns are shown in Fig. 1. Determination of ω_L leads directly to the observed field at the impurity, H_{obs}. The hyperfine field is then determined from the relation $H_{hf} = H_{obs} - H_{ext} + H_{DM}$, H_{ext} being the external applied field and H_{DM} the demagnetization field (0.8 kOe). Values of the hyperfine fields obtained are, in kilo-oersteds, H_{hf}(Ga*Co*) (77°K) = $-81.5(30)$; H_{hf}(Ge*Co*) (77°K) = $+46.5(12)$; H_{hf}(As*Co*) (306°K) = $+274(6)$. In these values, the correction for the Lorentz field is not included, and the errors include those of the nuclear g factors (see Table I).

The temperature dependence of H_{hf} was measured in the range $T = 77$ to ~900°K. The reliabil-

TABLE I. Excitation reactions and properties of nuclear probes.

Probe	Reaction	E_{exc} (keV)	E_γ (keV)	$T_{1/2}$ (nsec)	g factor
$^{68}_{31}$Ga	^{55}Mn(^{16}O, 2pn)	1230	120, 125 201, 605	60(2)	$+0.103(2)$[a]
$^{67}_{32}$Ge	^{54}Fe(^{16}O, 2pn)	734	734	70(7)	$-0.211(1)$[b]
$^{72}_{33}$As	^{59}Co(^{16}O, 2pn)	561	199	87(2)	$+0.116(2)$[c]

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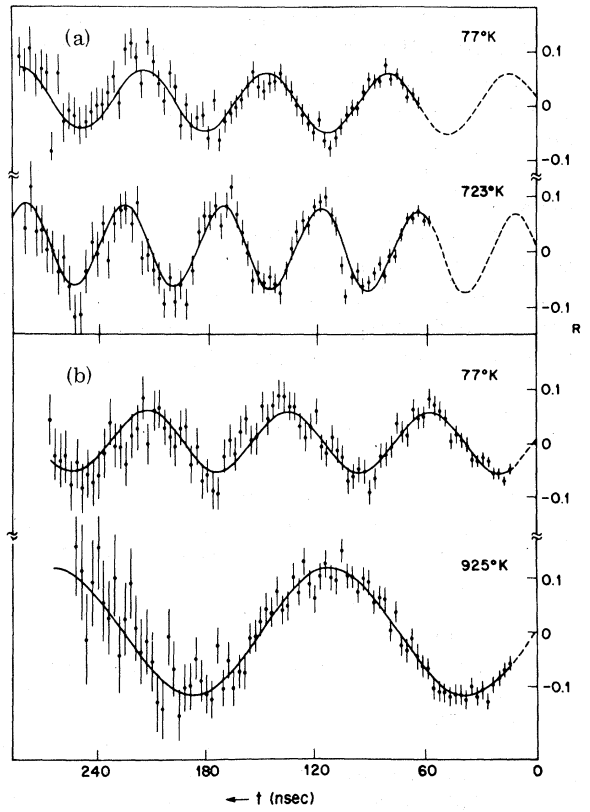

FIG. 1. Hyperfine nuclear precession of (a) ^{67}Ge and (b) ^{68}Ga in a Co single crystal at low and high temperatures. Note the *faster* precession for Ge in Co at high T and the *slower* precession for Ga in Co at high T.

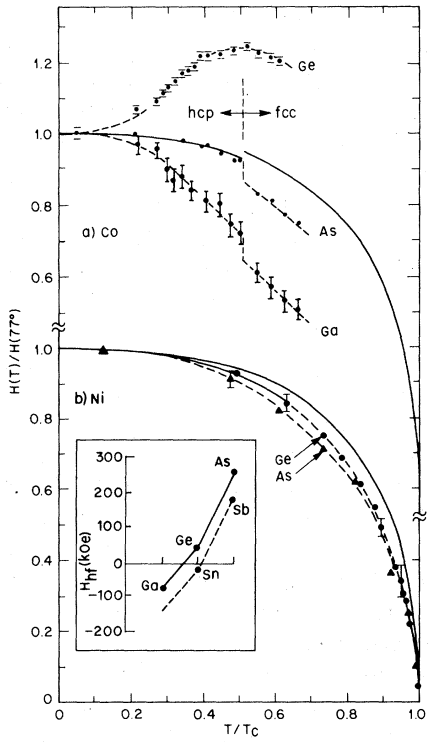

FIG. 2. Temperature dependence of the reduced hyperfine field $H_{hf}(T)/H_{hf}(77°)$ for various impurity elements in Co (curves *a*) and in Ni (curves *b*; data from Ref. 5). The errors on representative data points are only statistical errors of the ω_L measurements. The solid lines represent the reduced saturation magnetization $\sigma(T)/\sigma(0)$ of the hosts. The inset shows the systematics of H_{hf} at relevant impurities of the 4*sp* and 5*sp* series in Co.

ity of the temperature measurement was checked by the vanishing of the H_{hf} close to the Curie point of Ni (631°K) in previous experiments on $H_{hf}(T)$ in Ni performed with the same experimental arrangement. The main features of the $H_{hf}(T)$ results were carefully confirmed by measurements in which two impurity elements at a time were simultaneously excited by using composite targets (e.g., Mn and ^{54}Fe and Ga and Ge) and also by using the reactions in the Co-crystal backing which produces As impurities. Repeated measurements showed the $H_{hf}(T)$ data reported here to be well reproducible.

The observed $H_{hf}(T)/H_{hf}(77°)$ curves for a Co host are shown in Fig. 2(a). Included for comparison in Fig. 2(b) are results reported previously from this laboratory on $H_{hf}(T)/H_{hf}(77°)$ for Ge and As in a Ni host.[5] In Ni, the temperature curves for both As and Ge are closely similar and show a small deviation from $\sigma(T)/\sigma(0)$. This behavior appears to be typical for *sp* impurities in an Fe host also.[2,5] In marked contrast to Fe and Ni, the nature of $H_{hf}(T)/H_{hf}(77°)$ for these impurities in Co is quite unusual in that they are very different for Ga, Ge, and As.

The quality of the precession curves obtained throughout this work (see Fig. 1) indicates that all our results refer to implanted impurity nuclei being located at *unique* sites. That these are almost certainly substitutional lattice sites is indicated by the fact that Ga, Ge, and As are all known to be soluble in Co.[6] Present experience in implantation studies indicates that in such cases the implanted impurity always ends up at substitutional sites in the host.[7] Ion-channeling experiments are, however, being planned to obtain experimental proof of substitutionality of these implants in Co.

The unusual anomaly for $H_{hf}(T)$ in Ge*Co* discovered here invites comparison with the well-known anomaly[3] for the isoelectronic 5*sp* element Sn in Co. In that case, however, the nature of

the anomaly is quite different: H_{hf} *decreases* steeply with T and around $T/T_c \cong 0.5$ it even changes sign. But it must be pointed out that the sign of H_{hf}(Sn*Co*) is *negative* (~−22 kOe) while that of H_{hf}(Ge*Co*) is *positive* (~+46 kOe); the sign crossover is slightly shifted in phase in the two series for a Co host (see inset in Fig. 2). Thus one might expect an anomaly similar to H_{hf}(Sn*Co*) rather for Ga in Co and our data do indeed bear this out qualitatively. $H_{hf}(T)$ in Ga*Co* decreases rapidly although less steeply than for Sn. Thus Ga and Ge with hyperfine fields of opposite signs display strong anomalies which appear to be complementary to each other. In the case of As which has a large positive field (~+275 kOe), $H_{hf}(T)$ shows close scaling with $\sigma(T)/\sigma(0)$ up to $T/T \cong 0.5$ where the hcp → fcc phase transition occurs. At this point, however, there is a discontinuity and H_{hf} abruptly seems to scale with a normalization quite different from that of the fcc host magnetization. A discontinuity at the same point is observed also for $H_{hf}(T)$ in Ga*Co*. $H_{hf}(T)$ in Ge*Co* shows no discontinuity within experimental errors but does attain a maximum at this temperature.

Anomalies of the types reported here, together with that for Sn, *occur only in a Co host*;[8] they appear to be related to each other and occur systematically at well-defined elements in the 4*sp* and 5*sp* series. These clues, especially the latter, might indicate that their origin is connected intimately with the basic feature of these hyperfine fields, namely, the competition of the different contributive interactions. This special set of temperature anomalies of the hyperfine fields of *sp* elements at the points of sign crossover presents many distinctive features, which may provide for the first time sufficiently compelling criteria for a unique and common theory for these effects. It is to be hoped that this would lead to new knowledge especially about the origin of positive hyperfine fields which have been the subject of much debate.

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New Sequence of Structural Phase Transitions in Na_xWO_3

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Using precise lattice-parameter measurements, "cubic" Na_xWO_3 ($0.62 \leq x \leq 0.94$) has been found to transform from the ideal perovskite structure to three other related forms. The transition sequence is described in terms of a single vectorlike order parameter involving static in-phase tilts of WO_6 octahedra and is the zone-boundary analog of the ferroelectric series of transitions in $BaTiO_3$, the [001] tilt component arising from the condensation of the M_3 mode. Unexplained features of structural and Raman studies can now be interpreted.

The nonstoichiometric compounds Na_xWO_3 have recently attracted much attention because of their unusual electronic-transport properties. Of particular interest are the metal-nonmetal transition at $x \approx 0.2$,[1] the enhancement of the superconducting properties[2] around this composi-