prevailing three-step picture of the photoemission process has been reasonably successful. In this picture, the three stages, (1) optical excitation of electrons, (2) transport of some of these electrons to the surface, and (3) escape of some of these electrons across the surface, are considered to occur independently.

The measured photoelectric yield per incident photon was found to have a peak just below the plasma frequency and then drop sharply on passing through the plasma frequency. The simple model predicts that the yield per incident photon should be proportional to $(1-R)\alpha$. Values of $(1-R)\alpha$ obtained from the measured optical constants below 4 eV and plausible extrapolations above 4 eV showed the peaking effect and drop on passing through the plasma frequency similar to those in the yield. Our conclusion is that the variation of the yield can be understood in terms of the optical constants and the three-step model. We note that it was not necessary to invoke any sudden variation in the energy dependence of the mean free path.

The energy distributions of photoemitted electrons revealed a peak at the high-energy end which, in the three-step model, we identify as primary or unscattered electrons. The width of this peak was found to decrease with decreasing photon energy, an effect which can be understood in terms of the direct (i.e., **k**-conserving) nature of the optical excitation. A simple theory of direct transitions within the nearly free-electron model is able to explain the systematics of the width and height of the leading peak, but not its observed shape. The predicted shape is rectangular, whereas the observed shape is triangular. It remains to be seen whether this is due to an outright failure of the theory or the need to include extra effects such as lifetime broadening.

The region of the EDC's below the leading peak presents a kind of characteristic energy-loss spectrum. An intermediate piece of structure is observed in the EDC's for K, which we identify as a plasmon energy loss. This intermediate peak cannot be clearly discerned in Na, but is seen in our preliminary data on Rb and Cs, becoming progressively more pronounced and closer to the leading peak. These systematic trends are consistent with a plasmon interpretation. The separation of the intermediate peak and the leading peak in the latter metals leads us to prefer a surface, rather than a volume, plasmon loss.

Although we have interpreted our data solely in terms of the conventional three-step picture of the photoemission process, other possibilities cannot be ruled out. In fact, the very low values estimated for the electron-electron scattering length indicate that many-body effects are quite important. If so, it might be more appropriate to include the electron-electron scattering in the optical excitation process, as suggested by Nesbet and Grant[16] and by Sutton and Hopfield,[15] or in the setting up of the electronic states as done by Hedin, Lundqvist, and Lundqvist.[17] The similarity between the low-energy structure in the electron energy distribution predicted by the latter authors and the intermediate bump which we observe in the EDC's for K is particularly striking. However, it appears that this theory would require modification to accommodate surface plasmons in addition to volume plasmons.

ACKNOWLEDGMENTS

We would like to thank Galen B. Fisher for his help in analyzing the experimental data, and J. MacGowan and S. Wanner for their skilled work in constructing apparatus. We are grateful also for interesting discussions with Professor J. J. Hopfield and Leon Sutton, and our colleagues at Stanford.

PHYSICAL REVIEW VOLUME 188, NUMBER 2 10 DECEMBER 1969

Hyperfine Fields of Technetium and Zinc Impurities in Iron

P. INIA, Y. K. AGARWAL,* AND H. DE WAARD
Natuurkundig Laboratorium der Rijksuniversiteit, Groningen, The Netherlands
(Received 16 July 1969)

The magnetic hyperfine fields of technetium and zinc impurities in an iron lattice have been measured by perturbed angular correlation methods. The fields were found to be -400 ± 160 kOe for Tc in Fe and -105 ± 35 kOe for Zn in Fe. The accuracy is determined by that of the g factor of the intermediate state. The results fit well between the known values of the hyperfine fields of neighboring nuclei in iron.

I. INTRODUCTION

LARGE magnetic fields are often found at nuclei of nonmagnetic elements when these nuclei are embedded as dilute impurities in ferromagnetic metals.[1] These fields are of interest both for nuclear physics and for solid-state physics. Extensive use of these fields has been made in measuring the magnetic moments of

* On leave from Tata Institute of Fundamental Research, Bombay.

[1] B. N. Samoilov, V. V. Sklyarevskii, and E. P. Stephanov, Zh. Eksperim. i Teor. Fiz. **36**, 644 (1959) [English transl.: Soviet Phys.—JETP **36**, 448 (1959)].

vibrational states in nuclei.[2] Since these states have very short half-lives ($\approx 10^{-11}$ sec), measurements employing an external magnetic field are often not feasible. At present it is not possible to estimate the strengths of these internal fields from theory with any degree of accuracy. However, a qualitative understanding of the general trends of these fields, which has resulted from a systematic study, is now possible.[3]

In the present work the fields acting on technetium and zinc nuclei embedded in iron have been measured using perturbed angular correlation methods. In various previous measurements involving internal fields, there is doubt about the validity of the results due to one or both of the following two reasons. If the external field applied is too low to magnetize the foil to complete saturation, the full effect is not observed.[4] Furthermore, it is possible that a portion of the impurity atoms do not occupy the proper lattice sites; they may, for instance, be associated with vacancies or they may have formed clusters or compounds in the metal. Wrong results may then be expected. In the present work, special care was taken to avoid errors due to these two effects.

II. EXPERIMENTAL DETAILS

A. Method

In many cases, including the present, the unperturbed angular correlation of a γ-γ cascade can be written as[5]

$$W(\theta)=1+b_2\cos 2\theta, \tag{1}$$

where θ is the angle between the directions of the two γ rays. When a magnetic field is applied on the source, the interaction of the magnetic moment in the intermediate state with the magnetic field H causes a Larmor precession of the nucleus with a frequency given by the relation

$$\omega=-g\mu_N H/\hbar. \tag{2}$$

In this relation, g is the g factor of the intermediate state, and μ_N is the nuclear magneton.

In the case of integral measurements, with the magnetic field applied perpendicular to the correlation plane, the angular correlation can be expressed as[5]

$$W(\theta,\pm H)=1+\{b_2/[1+(2\omega\tau)^2]^{1/2}\}\times\cos(2\theta\mp\arctan 2\omega\tau), \tag{3}$$

where τ is the mean life of the intermediate state of the nucleus. Thus, from a measurement of the perturbed angular correlation pattern the value of the magnetic field H can be estimated if the values of g and τ are already known. It is also possible to estimate the value of H from a measurement of the quantity R defined as follows:

$$R=(C^+-C^-)/(C^++C^-), \tag{4}$$

C^+ and C^- being the coincidence rates for positive and negative directions of the magnetic field with the counters fixed at a definite angle θ. The quantity R is related to $\omega\tau$ by the relation

$$R=\pm b_2 2\omega\tau/[1+(2\omega\tau)^2], \tag{5}$$

where the positive sign occurs for $\theta=225°$ and the negative sign for $\theta=135°$. In the case of technetium, the complete angular correlation pattern was measured, while in the case of zinc only R was measured.

B. Apparatus

Conventional fast-slow electronics was used for the measurements. A description of the automatic angular correlation equipment has been given elsewhere.[6] A small C-core electromagnet, which produces a field of 1.2 kG, is used to magnetize completely the iron foils in the perturbed angular correlation measurements. The magnet poles, made of Armco iron, have a diameter of 2 cm and the pole tips have a truncated conical form to give best homogeneity of the field.[7] The gap width is 12 mm.

In the measurements on technetium the γ rays were detected in $1\frac{3}{4}\times 2$-in. NaI(Tl) crystals. Since for zinc the energies of the two γ rays in cascade are very close (206 and 185 keV), the 206-keV γ ray was detected in a Ge(Li) detector and the composite 206–185-keV peak was selected in the NaI(Tl) crystal in this case.

The NaI(Tl) detectors were carefully magnetically shielded with μ-metal shields surrounded by soft iron tubes so that the effect of the magnetic field on the counters was negligible. The distance from the source to the front of the NaI(Tl) crystals was 7 cm.

III. MEASUREMENTS AND RESULTS

A. Hyperfine Field at Technetium Impurities

The 40–141-keV γ-γ cascade in the 67-h decay of ^{99}Mo to ^{99}Tc was used. The g factor and the mean life of the 141-keV excited state in ^{99}Tc have recently been measured to be $g=+1.1\pm 0.35$ [8] and $\tau=277\pm 14$ psec.[9]

The sources for the perturbed angular correlation measurements were made by a metallurgical method. An Fe-Mo alloy, containing 0.7-at.% Mo, was prepared

[2] L. Grodzins, in *Hyperfine Structure and Nuclear Radiations*, edited by E. Matthias and D. A. Shirley (North-Holland Publishing Co., Amsterdam, 1968), p. 607. This book is hereafter referred to as HSNR.

[3] D. A. Shirley, S. S. Rosenblum, and E. Matthias, Phys. Rev. **170**, 363 (1968).

[4] B. I. Deutch, G. B. Hagemann, K. A. Hagemann, and S. Ogaza, in HSNR, p. 731.

[5] *Perturbed Angular Correlations*, edited by E. Karlsson, E. Matthias, and K. Siegbahn (North-Holland Publishing Co., Amsterdam, 1964).

[6] R. Sanders, thesis, University of Groningen, 1969 (unpublished).

[7] D. J. Kroon, *Laboratory Magnets* (Philips Technical Library, Eidhoven, 1968).

[8] F. C. Zawislak and J. D. Rogers, in HSNR, p. 151.

[9] P. Steiner, E. Gerdau, W. Hautsch, and D. Steenken, Z. Physik **221**, 281 (1969).

by melting together the proper quantities of well-mixed natural molybdenum and iron sponge in a high-frequency furnace. The solid solubility of Mo in Fe is about 5 at.%.[10] The alloy was then rolled to foils about 60 μ thick. The foils were annealed and homogenized at 700°C for about 4 h and next irradiated for 24 h in a thermal-neutron flux of 1.2×10^{14} n cm^{-2} sec^{-1} in the High-Flux Reactor at Reactor Centrum Nederland at Petten. The irradiated foils were annealed for about 24 h at 700°C.

Sources of $^{99}MoO_3$ were used for measuring the unperturbed correlation coefficient. The observed coincidence counting rates were normalized with respect to the single counting rates of both counters and corrected for chance coincidences and decay. A least-squares fit of the counting rate was made to Eq. (1). During three runs of two days each, about 18 000 coincidences per angle were collected, which gave an average $b_2=0.051\pm0.009$ (not corrected for geometry).

Using the alloy sources, the perturbed angular correlation pattern was measured. The observed coincidence counting rates were treated as mentioned above and least-squares-fitted to Eq. (3), treating b_2 as a constant and $\omega\tau$ as a variable. Figure 1 shows the results together with the fitted curves. Four runs of two days each and for both directions of the applied polarizing field gave $\omega\tau=+0.58\pm0.10$.

Using this value and the measured values of g and τ given above, the value of the magnetic field acting on technetium nuclei in iron is found to be $H=-400\pm160$ kOe. The error arises mainly from the error in the measured value of g. In Gerdau's group,[11] the magnetic field on Tc in Fe has recently been measured by the differential method on the 181-keV excited state in ^{99}Tc; their result is $H=-320\pm65$ kOe, in agreement with, but more accurate than, our value. The value of $\omega\tau$ from our measurement can be combined with the value of H obtained by Gerdau *et al.*[11] to give a slightly more accurate value of the g factor of the 141-keV excited state, $g_{141}=+1.36\pm0.34$.

B. Hyperfine Field at Zinc Impurities

The 206–185-keV γ-γ cascade in ^{67}Zn, excited in the decay of 78-h ^{67}Ga, was used for the measurement of the magnetic field on zinc nuclei in an iron lattice. The g factor and mean life τ of the 185-keV excited state have recently been measured by Lieder *et al.*[12] to be $g=+0.25\pm0.08$ and $\tau=1.45\pm0.07$ nsec. Natural-copper foils were bombarded with about 10-μA h, 24-MeV α particles in the cyclotron of the Instituut voor Kernfysisch Onderzoek at Amsterdam. ^{67}Ga is produced by the reaction ^{65}Cu(α,2n)^{67}Ga. The foils were used after a cooling-off period of about 24 h, so as to avoid

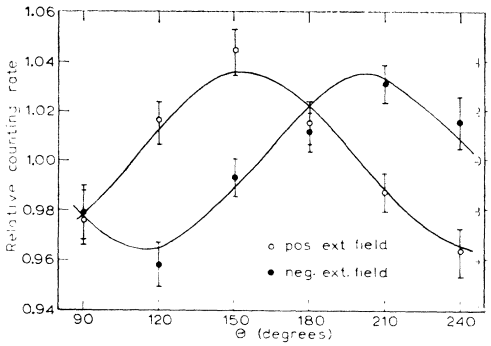

FIG. 1. Perturbed angular correlation of the 40–141-keV γ-γ cascade in ^{99}Tc. The source was in the form of a dilute alloy of Mo with Fe. The two curves correspond to the two directions of the external polarizing field.

interference from other gallium activities. The ^{67}Ga activity was separated from the bombarded foils by means of solvent extraction.[13] Liquid sources in the form of solutions of gallium chloride in dilute HCl were used to measure the unperturbed correlation coefficient. The data were treated as mentioned above for Tc. Five runs gave an average $b_2=-0.185\pm0.005$ (not corrected for geometry).

For the perturbed angular correlation measurements the gallium activity was electroplated on to a 100-μ-thick iron foil. The foil was then sealed in an evacuated quartz capsule and the activity was allowed to diffuse into the foil at 650°C for 40 h. The surface of the foil was thoroughly cleaned to remove any undiffused activity. The concentration of gallium in the iron foil was less than 0.1 at.%. The solubility of gallium in bcc iron is about 25 at.%.[14] Using these sources, the value of R defined in Eq. (4) was measured at angles $\theta=135°$ and $\theta=225°$. The values were then combined to give the mean value $|R|=0.058\pm0.005$. Using this value, the measured value of b_2 and the values of g and τ from Ref. 12, we obtain for the magnetic field on zinc nuclei in iron $H=-105\pm35$ kOe. In this case, as in the case of Tc, the major portion of the error arises from the uncertainty in the measurement of the g factor.

IV. DISCUSSION

For both cases that have been investigated, the Fermi contact interaction is the predominant source of the hyperfine field. Studies of the hyperfine field as a function of the atomic number of the impurity like those of Shirley *et al.*[3] indicate that the main possible contributions to the contact field are (i) conduction-electron polarization (CEP), (ii) overlap polarization (OP), and (iii) core polarization (CP). It follows from general arguments that CEP gives rise to a negative field at the impurity; detailed calculations—for instance, those

[10] *The Constitution of Binary Alloys*, edited by M. Hansen and K. Anderko (McGraw-Hill Book Co., New York, 1958).
[11] E. Gerdau *et al.* (private communication).
[12] R. M. Lieder, M. Fleck, K. Killig, M. Forker, K. H. Speidel, and E. Bodenstedt, in HSNR, p. 133.
[13] National Academy of Science Nuclear Science Series No. NAS-NS 3032, 1961, Procedure 1 (unpublished).
[14] S. Dasarathy and W. Hume-Rothery, Proc. Roy. Soc. (London) **A286**, 141 (1965).

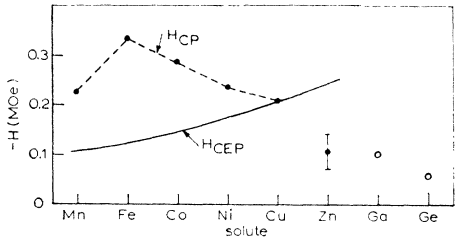

FIG. 2. Hyperfine fields versus atomic number for $3d$ and $4(s,p)$ solutes in iron. The solid line shows the CEP estimates of Shirley *et al.* (Ref. 3). The value for Zn is from the present work.

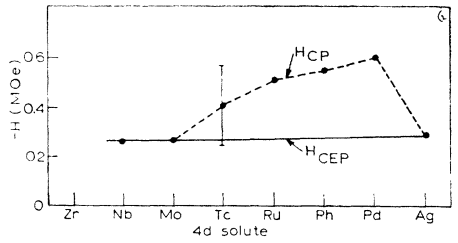

FIG. 3. Hyperfine field versus atomic number for $4d$ solutes in iron. The solid line shows the CEP estimate by Shirley *et al.* (Ref. 3). The value for Tc is from the present work.

of Watson and Freeman[15]—yield negative values also for CP, whereas the overlap contribution, on the other hand, is essentially positive. We shall consider the cases of Zn and Tc impurities in iron separately.

A. *Fe*Zn

The electron configuration of the outer shells of Zn is $3d^{10}4s^2$. If Zn is embedded in iron, it may be expected that the two valency $4s$ electrons are promoted to the conduction band while the more tightly bound $3d$ electrons remain *in situ*. Thus, the $3d$ shell is completely filled and cannot give rise to polarization of the inner-shell s electrons (CP). Furthermore, the radii of the $1s$ to $3s$ orbitals of Zn are so small that direct overlap with $3d$ orbitals of the surrounding iron atoms will be negligible. Therefore, we should concern ourselves primarily with the contribution of CEP. There exist no detailed calculations of this effect. Shirley *et al.*[3] have given an empirical expression from which approximate values of the CEP contribution for various elements can be derived [see their Eq. (13)]. These values are represented by the solid lines, marked H_{CEP}, in Figs. 2 and 3. The observed values of H for $3d$ and $4(s,p)$ solutes in iron are shown in Fig. 2. Extrapolation of the line in Fig. 2 yields $H_{\mathrm{CEP}}=-250$ kOe for *Fe*Zn, which is larger by a factor of 2 than our experimental value. It is seen that the expectation is about right for *Fe*Cu, but that the experimental value falls short by a factor of 2 for *Fe*Ga also. This may indicate that our assumption that both $4s$ electrons are completely delocalized is not true; if there is some remaining $4s$ density, direct overlap of these $4s$ electrons with iron $3d$ electrons may give rise to a positive contribution to the field that would reduce its total absolute value.

B. *Fe*Tc

If Tc, with an outer-shell electron configuration $4d^55s^2$, is embedded in iron, it may be assumed that it loses its $5s$ electrons to the conduction band. The partly filled $4d$ shell now has a resultant spin and magnetic moment that may be coupled to the $3d$ spins of the surrounding iron atoms by s-d exchange interaction. In this case, a CP contribution to the field may be expected apart from the CEP contribution. This is clearly illustrated in Fig. 3, in which the observed values of H have been plotted versus atomic number for the $4d$ group elements. Values of H expected for CEP only are indicated by the solid line marked H_{CEP}. Deviations from this line are present for Tc, Ru, Rh, and Pd. These are ascribed to CP. This part of the hyperfine field was expressed by Shirley *et al.*[3] as

$$H_{\mathrm{CP}}=2\langle S_z\rangle H_d, \tag{6}$$

where H_d is the CP hyperfine field arising from one paired d electron and $\langle S_z\rangle$ is the average z component of the spin. Freeman *et al.*[16] have calculated $H_{4d}=-370$ kOe. From the observed values of H and calculated values of H_{CEP} the value of H_{CP} can be estimated. This value of H_{CP} can then be combined with the value of H_{nd} to extract values of $\langle S_z\rangle$ and therefore of μ, the magnitude of the localized magnetic moment of the solute atoms. In several cases the values of μ thus calculated were found to be in good agreement with those derived from neutron scattering measurements by Collins and Low.[17] Following this procedure, a value $\mu=0.51$ is found for Tc. Unfortunately, Collins and Low have not measured μ for *Fe*Tc.

ACKNOWLEDGMENTS

The authors wish to thank Dr. S. Radelaar of the Laboratorium voor Metaalkunde of this University for making the Fe-Mo alloy, Miss J. C. Kapteyn of the Instituut voor Kernfysisch Onderzoek at Amsterdam for taking good care of the cyclotron irradiations, and F. ten Broek for performing the gallium separations. This work is partly supported by the "Stichting voor Fundamenteel Onderzoek der Materie" (FOM), subsidized by the Netherlands's Organisation for Pure Research (ZWO). One of the authors (YKA) wishes to thank FOM for the Research Fellowship which made possible his stay at Groningen.

[15] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2077 (1961).

[16] A. J. Freeman, B. Bagus, and R. E. Watson, Colloq. Intern. Centre Natl. Rech. Sci. (Paris) **164** (1966).

[17] M. F. Collins and G. G. Low, Proc. Phys. Soc. (London) **86**, 535 (1965).