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Te^{125} Mössbauer Effect in Paramagnetic and Antiferromagnetic $MnTe_2$†

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The Mössbauer effect associated with the 35.6-keV ($\frac{3}{2}\rightarrow\frac{1}{2}$) transition in Te^{125} is applied to extract the electronic structure and the induced magnetic features of the ditelluride ligand in antiferromagnetic $MnTe_2$ ($T_N=83.8$°K). Measurements above T_N at 90.1°K, reveal a quadrupole split spectrum with $|e^2qQ|=15.5$ mm/sec. Absorption spectra obtained below T_N result from a combination of a magnetic dipole interaction and a predominant electric quadrupole interaction with negative e^2qQ. At 4.2°K ($T/T_N=0.05$) and 20.3°K ($T/T_N=0.24$) the internal magnetic field $H=114\pm7$ kOe and the angle θ formed with q_{zz} is $30°{}_{-5}^{+3}$. At 77.3°K ($T/T_N=0.925$), $H=55\pm3$ kOe, and $0°\leq\theta<10°$. The sign and magnitude of the quadrupole coupling constant as well as the observed anisotropy in the recoilless fraction are consistent with the "molecular" conception of the Te^{1-}-Te^{1-} anion. Comparison of H in $(Te^{125})^{1-}$ and H in substituted $(I^{129})^{1-}$ (obtained from a separate experiment) suggests a transferred hyperfine interaction mechanism involving the unpairing of the ligand 5*s* orbitals. The resulting angle θ was found to be inconsistent with the suggested model of the spin arrangement as deduced from a neutron-diffraction pattern in powder samples by other authors.

I. INTRODUCTION

DATA on hyperfine structure in nuclei of nonmagnetic anions (ligands) are of primary interest not only for the understanding of the mechanisms involved in the transferred hyperfine interaction, but also for elucidating the role of a ligand in the magnetic superexchange.[1] The Mössbauer effect (ME) spectroscopy provides a powerful tool for determination of hfs parameters. In particular, the ME associated with the 35.6-keV transition in Te^{125} is the only method to obtain *both* the magnetic dipole and electric quadrupole coupling constants in tellurium ligands. Simultaneous determination of both these constants is of special interest in the case of the antiferromagnetic $MnTe_2$, the compound which is the subject of the present investigation.

Manganese ditelluride crystallizes in a fcc (pyrite) structure (see Fig. 1) with the Te_2 axes along the various body diagonals. Magnetic as well as crystal-chemical evidence[2] points to a possible ionic combination of Mn^{2+} and $Te_2{}^{2-}$ groups. Neutron-diffraction measurements performed at 4.2°K (Hastings, Elliott, and Corliss[3]) suggested a magnetic structure with an ordering of the "first kind" with spins parallel to the ferromagnetic planes. The Néel temperature was first reported by Sawaoka and Miyahara,[4] who deduced a value of T_N in the range of 80–90°K. Recently, I^{129} ME measurements[5] with a $MnTe_2{}^{129m}(\beta^-)\rightarrow I^{129}$ source extracted a more accurate value for T_N ($=83.8$°K).

The interesting and rather unusual feature of this antiferromagnet is the presence of Te^{1-}-Te^{1-} "molecular" anions. Assuming the ligand to be in a pure 2^- formal valency, invokes a large electric field gradient (efg) (produced by a *p* hole) acting at the Te^{125} nucleus, with its principal axis q_{zz} along the "molecular" σ_p bond. Also, the low-symmetry site of Te^{1-}, with three Mn^{2+} nearest neighbors, points to a possible "unpairing" of the outer electrons to ultimately produce a net spin density at the nucleus.

The purpose of the present investigation was to extract the various hfs parameters both in the paramagnetic and in the antiferromagnetic states, and subsequently to correlate them with the "molecular" properties of the ditelluride anion, with the features of the transferred hyperfine interaction, and also with the spin arrangement, thus providing additional information about the magnetic structure of this antiferromagnet.

II. EXPERIMENTAL

The $MnTe_2$ was prepared from natural abundant elemental Te and Mn. A stoichiometric mixture was

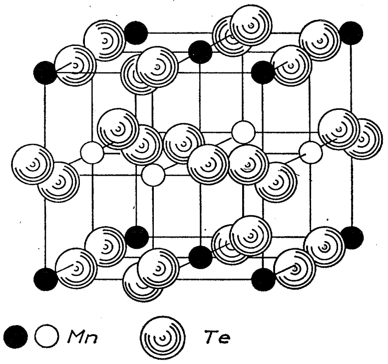

FIG. 1. The pyrite structure. Positive and negative orientation of the dipoles are shown by black and white spheres. The spin direction lies in the ferromagnetic planes. The Mn-Te, Te-Te distances and a_0 are 2.90 Å, 2.74(3) Å and 6.943 Å, respectively. The Mn-Te-Mn angle is 115.4° (see Ref. 3).

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sealed under vacuum in a quartz tube and heated to 600°C for seven days. A subsequent x-ray analysis showed no traces of Te impurities and other Mn-Te compositions. A polycrystalline, pulverized absorber $[t(Te^{125})=8.3\ \text{mg/cm}^2]$ was then prepared. The single-resonance line emitter, in this experiment, was the cubic $ZnTe^{125m}(T_{1/2}=58$ days) prepared by heating under vacuum to 900°C, for 24 h, a stoichiometric mixture of Zn and neutrons activated Te enriched with Te^{124}.

All the measurements were performed at low temperatures, in a double Dewar vacuum cryostat with both source and absorber immersed in cryogenic liquids (L). The temperatures covered were 90.1°K (LO_2), 77.3°K (LN_2), 20.3°K (LH_2), and 4.2°K (LHe). The 35.6-keV γ ray was analyzed with a 0.1-mm-thick NaI(Tl) scintillator attached to an EMI 9514-AS photomultiplier by detecting the 7-keV escape peak. This method of detection was necessary to overcome the intense Te K x-ray ($E_K\sim 28$ keV) radiation resulting from the metastable decay and from the internal conversion of the 35.6-keV transition. A constant acceleration Doppler velocity applied to the source was provided by a Kankeleit system[6] and counts were stored in a 400-Intertechnique multichannel analyzer, operated in time mode, with forward-backward address scaler.[7] Experimental results are depicted in Fig. 2.

III. ANALYSIS OF SPECTRA

A. Paramagnetic State

The absorption spectrum measured at 90.1°K ($T>T_N$) is depicted in Fig. 2(a). It is composed of a doublet, resulting from a pure quadrupole interaction in the $I=\frac{3}{2}$ excited state. A computer least-squares fit to the experimental points was carried out, keeping the linewidth, quadrupole splitting, isomer shift, intensities, and background as variable parameters. The results are given in Table I. A pertinent feature in the spectral shape is the unequal intensity of the absorption peaks. This phenomenon when observed in a polycrystalline sample is due to the anisotropic recoilless fraction and is commonly referred to as the Karyagin effect.[8] Unfortunately, in the case of spin $\frac{3}{2}$, the asymmetry parameter of the efg $\eta=(q_{xx}-q_{yy})/q_{zz}$ cannot be measured independently, and it is incorporated in the quadrupole splitting parameter. But owing to considerations to be discussed in Sec. IV, one may neglect η in the present case. This hypothesis considerably simplifies the analysis of spectra obtained in the antiferromagnetic state which now we proceed to describe.

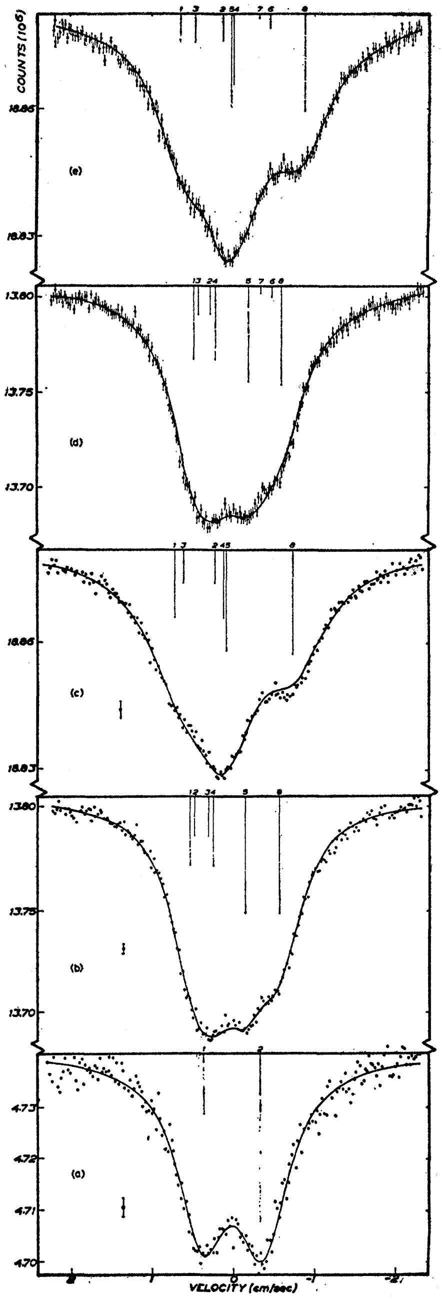

FIG. 2. Te^{125} Mössbauer-effect absorption spectra at the paramagnetic and antiferromagnetic states. (a) $T=90.1$°K ($T/T_N=1.07$). Spectrum corresponding to pure quadrupole splitting. Solid line shows the computer least-squares fit. (b) $T=77.3$°K ($T/T_N=0.925$). Spectrum involving both magnetic and quadrupole interaction. Solid line shows the computer least-squares fit assuming $\theta=0$. (c) $T=4.2$°K ($T/T_N=0.05$). Solid line shows the computer least-squares fit with $\theta=0$. (d) Same as (b). The solid line is a theoretical spectrum with the same hfs parameters as obtained in (b) but $\theta=30°$. (e) Same as (c). Solid line is a theoretical spectrum with $R=2.1$, $2\Gamma=8.5$ mm/sec, and $\theta=30°$. The transitions assignment follows the ordering shown in Fig. 4.

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TABLE I. Mössbauer-effect spectroscopic parameters of $MnTe_2^{125}$ at the paramagnetic and antiferromagnetic state as deduced from the least-squares-fit analysis. Values given in italics are the adopted values for the lowest temperature measurements (see text). The parentheses correspond to the uncertainty in the last figure. Results obtained at 20.3 and 4.2°K are identical, within the experimental errors. The value of e^2qQ given at $T/T_N<1$ were used as a fixed parameter. The magnetic coupling constant as well as R are related to the $I=\frac{3}{2}$ level magnetic moment.

Temp. °K	T/T_N	e^2qQ (mm/sec)	μ^*H (mm/sec)	R $-e^2qQ/4\mu^*H$	H (kOe)	2Γ (mm/sec)	i.s. (mm/sec)	θ (deg)	ρ
90.1	1.07	−15.5(2)	···	···	···	8.0(3)	0.0(4)		0.95(3)
77.3	0.92	−15.5	0.88(2)	4.4	55(3)	7.5(3)	0.2(4)	$0\le\theta<10$	0.90(4)
4.2	0.05	−15.5	1.69(3)	2.3	106(5)	9.2(3)	0.0(4)	0	···
20.3	0.24		*1.80(9)*	*2.1*	*114(7)*	*8.5(2)*	**0**	30_{-5}^{+3}	···

B. Antiferromagnetic State

Absorption spectra recorded at 77.3°K ($T/T_N=0.92$) and 4.2°K ($T/T_N=0.05$) are shown in Figs. 2 (b) and 2 (c). The spectrum corresponding to 20.3°K (LH_2) is not presented here, since it is identical—within the statistical errors—to that measured at 4.2°K. One immediately observes the significant change in the spectral shape when crossing the Néel temperature. This change is a result of the transferred magnetic interaction at the Te^{125} nuclei. Previous to the spectra analysis, we carried out calculations to simulate absorption spectra characterized by various values of quadrupole coupling to magnetic coupling ratio (R), and θ the angle formed by q_{zz} (the principal axis of the efg) and the internal magnetic field H. This was carried out by means of a computer and was based on the solutions of a spin Hamiltonian $\mathcal{H}$ combining both the electric quadrupole interaction $\mathcal{H}_Q$ and the magnetic dipole interaction $\mathcal{H}_M$, namely,

$$\mathcal{H}=\mathcal{H}_Q+\mathcal{H}_M\,, \tag{1}$$

where

$$\mathcal{H}_Q=\{e^2q_{zz}Q/[4I(2I-1)]\}[3I_z^2-I(I+1)]\,, \tag{2}$$

$$\mathcal{H}_M=\mu H[I_z\cos\theta+I_x\sin\theta]/I\,. \tag{3}$$

In that case the quantization axis was purposely chosen to coincide with the axial symmetric q_{zz}. The quadrupole interaction applies only for the $I=\frac{3}{2}$ excited state and, in general, the matrix described by (3) will have also off-diagonal elements, corresponding to terms represented by $I_x\sin\theta$.

In the simulation of theoretical spectra we used the known values of the ground-state ($\mu=-0.887\mu_N$[9]) and excited-state [$\mu^*=0.60(2)\mu_N$[10]] magnetic moments, and the linewidth obtained from the 90.1°K experiment, properly reduced, to account for the effective thickness of the eight peaks of the magnetic-quadrupole split spectrum. Typical spectra for different values of $R(=-e^2qQ/4\mu^*H)$ and θ are shown in Fig. 3. The intensities of the lines were obtained from the solution of $\mathcal{H}$ as described by (1)-(3), using the proper squares of the Clebsch-Gordan coefficients, averaging over the angle between q_{zz} and the γ-ray direction, and assuming an isotropic recoilless fraction. The resonance line shapes were Lorentzian of width 2Γ.

From observation and comparison with the experimental spectra, the following preliminary conclusions were drawn: (i) The strength of the quadrupole interaction exceeds that of the magnetic interaction ($|R|>1$), (ii) e^2qQ is negative, and (iii) values of θ corresponding to spectra recorded at LHe and LN_2 cannot be larger than 30° and 10°, respectively. With those starting points we proceeded to analyze the LN_2 spectrum.

As a first approximation, we assumed $\theta=0°$. In that case, the off-diagonal elements in (3) vanish and the six-lines spectrum can be analyzed using the relation of the energy positions E_{ij}.

$$E_{ij}=-\mu H[(\mu^*/\mu)m_j^*/I^*-m_i/I]\pm e^2qQ/4+\text{i.s.}\cdots\,, \tag{4}$$

where * stands for the excited state, $+e^2qQ/4$ corresponds to $m_j^*=\pm\frac{1}{2}$, and $-e^2qQ/4$ corresponds to $m_j^*=\pm\frac{3}{2}$. The solid line through the experimental

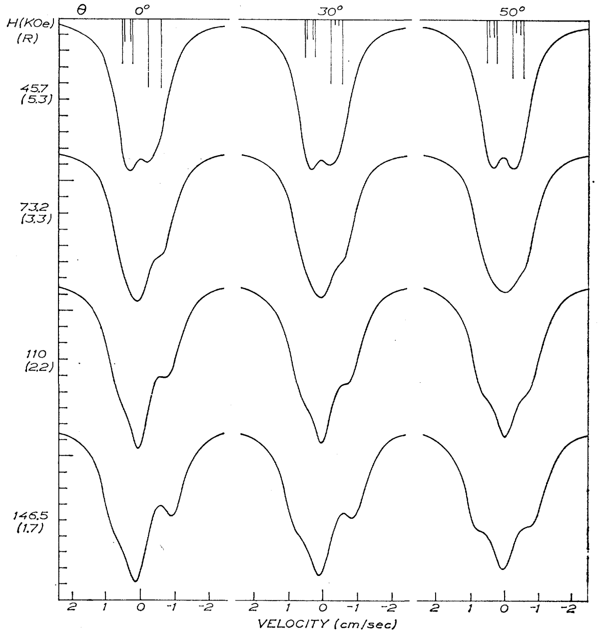

FIG. 3. Typical simulated ME absorption spectra for Te^{125} incorporating both magnetic dipole and axial symmetric electric quadrupole interactions for different values of θ and $R(=-e^2qQ/4\,\mu^*H)$. $2\Gamma=8.0$ mm/sec.

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points in Fig. 2 (c) is a result of a least-squares fit, restricting the six-lines position by Eq. 4, and requiring the same linewidth for all components, and the intensities to be proportional to the square of the Clebsch-Gordan coefficients. The value of $e^2qQ/4$ was fixed to the value deduced for the paramagnetic state. The variable parameters were μH, isomer shift (i.s.), linewidth, the ratio ρ of intensities of the two groups of lines specified by $\Delta m=0$ and $\Delta m=\pm 1$ (to account for the Karyagin-Goldanskii effect), and background.

The computed least-squares-fit parameters are given in Table I. Also here, as in the pure quadrupole spectrum, the intensity of transitions specified by $\Delta m=\pm 1$ are enhanced with respect to those specified by $\Delta m=0$. The fit to the experimental points, with theoretical spectra computed with $\theta>0°$, was unsuccessful. In Fig. 2 (d) a simulated spectrum for $\theta=30°$ is displayed through the experimental points. This curve, computed with the same values of R (4.4) and linewidth as obtained from the analysis with $\theta=0°$, clearly deviates from the points particularly in the -0.5–0-cm/sec range. The extent of the deviation increases with θ. The reason is mainly the appearance of the forbidden lines (6 and 7) resulting from mixed $|m^*\rangle$ states in the $I=\frac{3}{2}$ level. The extent of mixing increases with $\sin\theta$ [see Eq. (3)], and this significantly affects the transition intensities. An illustration for the effect of θ in the spectral shape is given, in more detail, in the upper part of Fig. 3. Because of the relatively large value of R, the *position* of the lines will be barely affected by change in θ. It can be shown[11] that the first- and second-order Zeeman perturbation of the quadrupole terms $E^{3/2}$ and $E^{1/2}$ (see Fig. 4) are

$$E^{3/2}(\pm)=e^2qQ/4\pm\mu H\cos\theta+\tfrac{2}{3}(\mu H\sin\theta)^2/e^2qQ$$

and

$$E^{1/2}(\pm)=-e^2qQ/4\pm\tfrac{1}{3}\mu H(1+3\sin^2\theta)^{1/2}-\tfrac{2}{3}(\mu H\sin\theta)^2/e^2qQ\,, \quad (5)$$

where $\pm$ corresponds to $+m$ and $-m$ sublevels when $\theta=0$. For the present value of R, an increase in θ from 0° to 40° will alter the values of E by only 2%. It was found that slight deviations from the absorption linewidth do not affect appreciably the spectral shape, yet changes in H, even by a small fraction, affect the total breadth of the spectrum, the reason being the ground-state splitting. The extra sensitivity of the spectral shape to θ and its breadth to H allowed us to confine the values of these parameters as given in Table I.

Procedures similar to those described above were carried out with the LHe (and LH$_2$) spectrum. First a least-squares-fit analysis was carried out by assuming $\theta=0$. However, in that case the fit quality was unsatisfactory [see Fig. 2 (c)], particularly in the 0.2–0.8-cm/sec and (-0.5)–(-1.0) cm/sec ranges. Moreover, the linewidth deduced from the computation was too broad to account for the mere increase in the absorber effective thickness with decrease in temperature. In Fig. 2 (e) we show a theoretical spectrum computed with $R=2.1$, $\theta=30°$, and $2\Gamma=8.5$ mm/sec, where the proper parameters were chosen to provide the optimal fit with the experimental points. The better quality of this fit strongly suggests an angle of approximately 30° between q_{zz} and H_{eff}. In this case, because of the low temperature where the Karyagin-Goldanskii effect decreases, we assumed $\rho=1$.

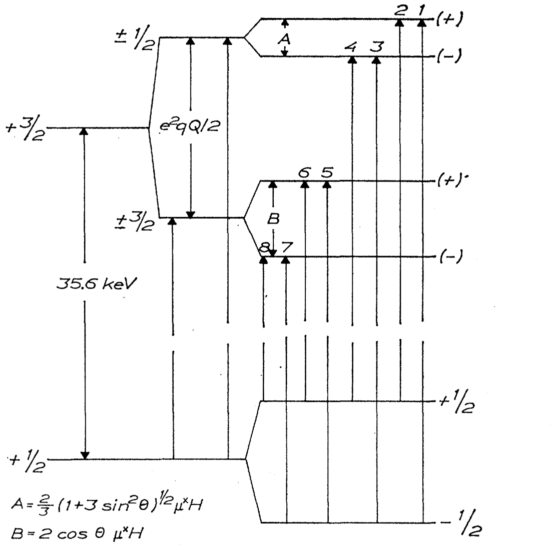

FIG. 4. Hyperfine interaction in the $I=\frac{3}{2}$ and in $I=\frac{1}{2}$ nuclear states in Te^{125}. The splitting separation of the combined magnetic and quadrupole interactions is proportional to the actual hfs parameters measured at LHe.

IV. DISCUSSION AND CONCLUSIONS

A. Molecular Nature of the Te$_2^{2-}$ Anion

If MnTe$_2$ is composed of pure ionic groups of Mn^{2+} and Te$_2^{2-}$ ions, the latter will have an electronic configuration identical to that of molecular iodine. In that case the outer shell of Te^{1-} is $5s^25p^5$, namely, one p electron lacking to complete the spherically symmetric $5p^6$ Xe shell. As shown in the case of I$_2$,[12] such a "p hole" in the Xe shell produces an efg with magnitude identical to that due to one p electron in the lowest $5p$ state but with a positive sign. Unfortunately, calculations of the efg for Te $5p^5$ configuration are not available; however, one should expect a value very close to that found for elemental Te.[13]

Measurements at the antiferromagnetic state yield a negative sign of e^2qQ and since Q is negative,[14] *the efg*

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is positive. Furthermore, the quadrupole coupling constant is identical in magnitude with that measured for elemental Te^{125} by Violet *et al.*[13] [$e^2qQ=1.52(4)$ cm/sec] and Stepanov *et al.*[15] (1.55 cm/sec). We then conclude that in Te_2^{2-} the "intramolecular" bonding is along the molecular axis and the outer configuration is $5s^25p^5$ where the p hole is along the σ bond. This, consequently, supports the previous evidence[2] for a pure ionic combination of Mn_2^{2+} and Te_2^{2-}. The low-symmetry site of Te^{1-} and a slight covalency mixture with the Mn neighbors could, in principle, reduce the value of q_{zz} and also distort the axial symmetry of the efg. But, recent ME measurements in $(I^{129})^{1-}$ substituting Te^{1-} in $MnTe_2$ showed evidence that the efg due to the above-mentioned properties is about 4% of the efg produced by a p hole. This value can be regarded as an estimate for q_{xx} (or q_{yy}) in $(Te^{125})^{1-}$ and therefore as an upper limit for η.

Additional evidence for the Te_2^{2-} molecular nature is provided by the anisotropy of the recoilless fraction. From Fig. 2 (a) it can be seen that the intensity of the absorption peak designated by $-2-$ and corresponding to the $\pm\frac{3}{2}\rightarrow\pm\frac{1}{2}$ $(\Delta m=1)$ transition is relatively larger than that corresponding to $\pm\frac{1}{2}\rightarrow\pm\frac{1}{2}$. The present observation results from the superposition of an anisotropic $f(\theta)$ with the angular dependence of the nuclear dipoles specified by $\Delta m=\pm1$ and $\pm\frac{1}{2}\rightarrow\pm\frac{1}{2}$, respectively. Assuming an axial symmetric mean-square displacements $\langle x^2\rangle$.

$$\langle x^2\rangle(\theta)=\langle x^2\rangle_{\parallel}\cos^2\theta+\langle x^2\rangle_{\perp}\sin^2\theta\,, \tag{6}$$

where $\parallel$ and $\perp$ denote parallel and perpendicular with respect to q_{zz}, it can be shown[16] that the ratio ρ of the intensities of the two peaks will be

$$\rho\equiv\frac{I(\frac{1}{2}\rightarrow\frac{1}{2})}{I(\Delta m=1)}=\frac{1}{3}\left(\int_0^1 e^{-k^2\alpha\cos^2\theta}(5-3\cos^2\theta)d(\cos\theta)\right)\Bigg/\left(\int_0^1 e^{-k^2\alpha\cos^2\theta}(1+\cos^2\theta)d(\cos\theta)\right), \tag{7}$$

where $\alpha=\langle x^2\rangle_{\parallel}-\langle x^2\rangle_{\perp}$, k is the γ-ray wave number, and $\frac{3}{2}(1+\cos^2\theta)$ and $\frac{1}{2}(5-3\cos^2\theta)$ are the $\Delta m=\pm1$ and $\pm\frac{1}{2}\rightarrow\pm\frac{1}{2}$ angular dependence, respectively. ρ is normalized to unity when $\alpha=0$. Whenever $\rho<1$, α is negative, namely, $\langle x^2\rangle_{\perp}>\langle x^2\rangle_{\parallel}$.[16] In the present case, $\rho=0.95(3)$, which means that $f=e^{-k^2\langle x^2\rangle}$ parallel to the covalent Te^{1-}-Te^{1-} bond axis is larger than that directed towards the various Te-Mn ionic bondings.

B. Transferred Hyperfine Interaction

The effective magnetic field H measured in Te^{125} expresses the extent of overlap—at the Te^{1-} site—between the Te_2^{2-} molecular orbitals and the $3d$ Mn^{2+} nearest-neighbor wave functions. It is instructive to compare this field with that measured at I^{1-} substituting Te^{1-}. Recent I^{129} ME measurements[5] yield $H_{\text{sat}}(I^{1-})=215(1)$ kOe, namely, an increase of about a factor of 2. The same trend of increase in H with increase in Z, is found in $\mathit{Fe}Te^{125}$ (Ref. 10) and $\mathit{Fe}I^{129}$ (Ref. 17). Also, in this case the increase is about a factor of 2. This common trend is compatible with the mechanism of transferred hyperfine interaction as suggested by Shirley[18] which involves direct overlap between the $5s$ outer shell of the ligand orbital with the $3d$ orbital of the magnetic cations. We find an opposite trend in H for instance, when the ligand is coordinated with the $Cr^{3+}t_{2g}$ orbitals. As suggested by Pasternak and de Waard,[19] the transferred hyperfine interaction in that case is attributed to unpairing of the π_p orbitals of the ligands due to covalency mixture with the $3d_{\pi}Cr^{3+}$ orbitals.

Valuable data obtained in the present investigation concern the orientation of H in respect to q_{zz}, or equivalently, in respect to the various body diagonals. The following experimental facts are obtained. (i) There is a unique angle θ, formed by the Te_2^{2-} axis and H. (ii) This angle is in the vicinity of 30° at low temperatures and very close to 0° near the critical point. We now try to correlate these facts with the known magnetic structure, with the assumption that the Te^{125} polarization direction is collinear with the direction of the resultant magnetization at the Te^{1-} site. Neutron-diffraction data[3] of powder samples at LHe temperature indicate a magnetic ordering which follows the chemical unit cell and with spins along the ferromagnetic planes (see Fig. 1). If the spins form correlated sublattices, $H(Te^{125})$ will be collinear with the spin directions. From the structure of the chemical unit cell, it is clear that only when the spins are directed along the cube edges will there be a unique angle ($\theta=55°$) in respect to the various Te_2^{2-} axis directions. However, an angle of 55° contradicts the actual experimental spectral shapes, depicted in Fig. 2. The reader is referred to Fig. 3, last column, where simulated spectra with $\theta=50°$ are shown for different values of R. Moreover, if the spins are not directed, say, towards [010] but in another direction within the ferromagnetic plane, there will always be two distinct angles with respect to the Te_2^{2-} axis, ultimately resulting in a complex absorption spectrum. A possible conclusion is that the spins are arranged in a more complex formation. For instance, an antiferromagnetic structure with a "screw-type" arrangement as proposed by Yoshimori[20] for the rutilelike MnO_2 could in principle lead to a unique angle of ~30° at LHe in respect to the various body diagonals. In Yoshimori's model, the "pitch of

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the screw" (and θ) will depend on the J_2/J_1 ratio, where J_1 and J_2 are, respectively, the first and second neighbor exchange integrals. This model could also explain the two values of θ obtained near T_N and at low temperatures, since the value of J_2/J_1 could be different near the critical point and at saturation. In order to verify the applicability of the screw-type model in this case, it is, however, necessary to carry out neutron diffraction with single crystals.

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Electron Spin Polarization around a Magnetic Impurity Using the Takano and Ogawa Theory of Kondo's Effect[*]

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The conduction-electron spin polarization induced by a localized spin in a metal has been calculated using the Takano and Ogawa theory of the quasibound state. The theory predicts a positive contribution to the polarization at the impurity nucleus due to the *s-d* interaction for temperatures lower than T_K, the transition temperature, and an oscillatory spin polarization of conduction electrons about the impurity at all temperatures. The oscillatory spin polarization is of the Ruderman-Kittel-Kasuya-Yosida form, but it is proportional to S^Z, the effective temperature-dependent spin which appears in the expression for the impurity contribution to the magnetic susceptibility. A comparison of theory with experiment is made for several "spin-compensated" systems with particular emphasis on Au-V and Cu-Fe alloys.

I. INTRODUCTION

OF considerable importance in the study of the ground state of magnetic impurities in metals is the question of how the Kondo effect will manifest itself in the conduction-electron spin polarization around a localized spin. Because of the divergence in perturbation theory at low temperatures, one would not expect the Born approximation for the polarization (associated with the names Ruderman, Kittel, Kasuya, and Yosida, and thus referred to as RKKY) to be valid.[1]

Several authors have investigated this question. Suhl, using S-matrix theory, deduced that the spatial dependence of the electron spin polarization would be unaffected at distances $r \gg 1/k_F$ from the impurity atom.[2]

Fullenbaum and Falk calculated the spin polarization $p(r)$ by extending the Nagoaka equations of motion[3] to the case where rotational symmetry is destroyed by a magnetic field.[4] A perturbational solution of the set of equations led them to an expression for $p(r)$ which involves not only the RKKY term but an additional term proportional to $J\ln(k_F r)$. This was interpreted as a manifestation of the Kondo effect in $p(r)$.

This treatment was extended by Everts and Ganguly[5] who found that the RKKY term $p_0(r)$ was proportional to the average of an effective spin rather than the bare impurity spin, the effective spin also entering into the static susceptibility χ.

Finally, Heeger *et al.*[6] calculated the polarization on the basis of the Applebaum-Kondo approach to the ground state.[7] They also found the modified RKKY polarization $p_0(r)$. However, in addition to that they also obtained a negative term which varies as $[\sin(2k_F r)/r]^2$.

In this paper, we investigate the spin polarization about a magnetic impurity using the solutions of the Takano and Ogawa theory of the Kondo effect.[8] These authors have solved a truncated set of Green's function equations for the *s-d* exchange Hamiltonian using the Gor'kov method in the theory of superconductivity. Certain averages are taken out, which imply the existence of a bound state between the localized spin and spin density of conduction electrons for both signs of J, the exchange integral. In a recent paper, their calcu-

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